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Ab Initio Characterization of Triatomic Bromine Molecules of Potential Interest in Stratospheric Chemistry

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The equilibrium structures, harmonic vibrational frequencies, quadratic force fields, dipole moments, and IR intensities of several triatomic bromine compounds of known or potential importance in stratospheric ozone depletion chemistry have been determined using the CCSD(T) electron correlation method in conjunction with a basis set of triple zeta double polarized (TZ2P) quality. Specifically, the molecules included in the present study are HOBr, HBrO, FOBr, FBrO, BrNO, BrON, Br_2O, BrBrO, BrCN, BrNC, ClOBr, ClBrO, and BrClO. Very accurate isomeric energy differences have also been determined at the CCSD(T) level with atomic natural orbital basis sets that include through g-type functions. In most cases, the isomer with a normal neutral Lewis dot structure is the lowest energy form, with the single exception that FBrO is predicted to be 11.1 kcal/mol (0 K) lower in energy than FOBr. In all cases, however, the hypervalent isomer is more stable relative to the isomer with a normal Lewis dot structure as compared to the chlorine analogs. Consistent with this observation, the energy of the last three molecules given above increases in the order ClOBr < ClBrO < BrClO. The CCSD(T)/TZ2P geometries and vibrational frequencies are in good agreement with the available experimental data. Heats of formation are determined for all species using a combination of theoretical isomeric, homodesmic, and isodesmic reaction energies. The accuracy of these quantities is ultimately dependent on the reliability of the experimental heat of formation of HOBr.

Introduction

There is growing interest in developing a more complete understanding of stratospheric chemisty, especially halogen and nitrogen oxide chemistry that leads to ozone depletion. As such, there has been considerable work over approximately the last 30 years aimed at better characterizing chlorine, fluorine, and nitrogen oxide molecules that are prevalent in the stratosphere. Over the last few years this laboratory has been involved in the *ab initio* characterization of several chlorine, fluorine, and nitrogen oxide species (e.g., see refs 1–5 and references therein). Although bromine is a minor constituent of the stratsophere, it is known to have a greater ozone depletion potential than chlorine (for example, see refs 6 and 7, and references therein). Until fairly recently, however, bromine compounds have attracted much less interest, and the present *ab initio* study is designed to provide a better characterization of triatomic bromine-containing oxide compounds that are of potential or known importance in stratospheric chemistry. Specifically, the HOBr, FOBr, BrNO, BrON, Br_2O (i.e., BrOBr), BrCN, BrNC, and ClOBr molecules and the hypervalent HBrO, FBrO, BrBrO, ClBrO, and BrClO compounds have been studied via *ab initio* calculations in the present investigation.

Nitrosyl bromide, BrNO, is probably the best experimentally characterized of the molecules included in this study. The vibrational spectrum,[8,9] microwave spectrum and molecular structure,[10–12] electronic spectrum,[13] and heat of formation[14] of BrNO have all been the subject of previous investigations. At this point, the gas-phase fundamental vibrational frequencies and a vibrationally averaged molecular structure are both well established and therefore BrNO will serve as a benchmark for evaluating the reliability of *ab initio* geometries and frequencies for bromine oxide molecules that are obtained with the singles and doubles coupled-cluster method that includes a perturbational estimate of the effects of connected triple excitations, CCSD(T),[15] in conjunction with a one-particle basis set of triple zeta double polarized (TZ2P) quality. The heat of formation of BrNO is reported to be well established,[14] and this will enable us to determine accurate heats of formation for other bromine compounds using a combination of isomerization and isodesmic *ab initio* reaction energies together with some experimental data on chlorine compounds. We are aware of only one previous *ab initio* study on BrNO in which the effects of electron correlation were explicitly included. Meredith, Quelch, and Schaefer[16] studied both the BrNO and BrON isomers at the singles and doubles configuration interaction (CISD) level of theory using a double zeta polarized basis set. Their CISD/DZP equilibrium geometry was in modest agreement with the experimental structure, with the theoretical Br–N bond distance too short by ≈0.04 Å. In the earlier studies of chlorine oxide species[1–5] the CCSD(T) level of theory has proven to yield equilibrium geometries and vibrational frequencies that are generally more accurate than those at the CISD level of theory.[17]

The HOBr and BrCN molecules are the next most studied bromine triatomics included in this study. These are the only other species for which vibrationally averaged structures[18–20] and all fundamental vibrational frequencies[20,21] have been experimentally observed or deduced. The heat of formation of HOBr has also been examined in several recent investigations,[22–24] but the variation among these values is rather large. This is discussed in more detail later. We are aware of only one previously published *ab initio* study of HOBr in which the effects of dynamic electron correlation were included. In this study, McGrath and Rowland[22] determine a $\Delta H^\circ_{f,300}$ value of −14.2 kcal/mol using G2 theory, although they do not specify the one-particle basis set that was used for bromine. Furthermore, G2 theory[25] was not designed for molecules containing third-row atoms (such as bromine) and therefore this value must be viewed with caution. For BrCN, we are aware of only one previous *ab initio* study in which the effects of electron correlation were explicitly included. Kellö and Sadlej[26] exam-

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ined the electrical properties of the cyanogen halides (F, Cl, Br, and I) using large basis sets, sophisticated coupled-cluster electron correlation methods, and experimental geometries. They showed that relativistic effects do not become significant until ICN.

Some of the fundamental frequencies of Br_2O, BrBrO, BrNC, BrClO, and ClBrO have been observed experimentally[21,27] and these are discussed further below. Properties determined in the present investigation include equilibrium geometries, dipole moments, harmonic vibrational frequencies, infrared (IR) intensities, isomerization energies, and heats of formation. The *ab initio* methodology used in this study is discussed in the next section and the results and discussion are presented in the following section. Conclusions are presented in the final section.

Computational Methods

The equilibrium geometries were determined with a TZ2P basis set at the CCSD(T) level of theory. The TZ2P basis set used for the C, N, O, and F atoms consist of Dunning's[28] 5s3p contraction of Huzinaga's[29] 10s6p primitive sets, and the H 3s/5s set comes from the same source. The polarization orbital exponents (two p functions for H and two d functions for C, N, O, and F) are taken from Dunning.[30] The Cl TZ2P basis set consists of McLean and Chandler's[31] 6s5p contraction of Huzinaga's 12s9p primitive set augmented with two sets of polarization functions with exponents, $\alpha_d = 1.072$ and 0.357. The Br TZ2P basis set is composed of a 6s5p2d contraction of a 17s13p6d primitive set as given by Schaefer, Huber, and Ahlrichs.[32] The orbital exponents of the two d polarization functions are $\alpha_d = 0.674$ and 0.225. All six components of the Cartesian d functions were included in the basis sets. Coupled-cluster analytical gradient methods[33,34] were used to locate equilibrium structures, while quadratic force constants, harmonic frequencies, and IR intensities were determined by finite differences of analytical gradients. The dipole moment was determined as the derivative of the energy with respect to an external electric field. In all coupled-cluster calculations, the C, N, O, and F 1s-like core molecular orbitals, the Cl 1s- and 2sp-like core molecular orbitals, and the Br 1s-, 2sp-, and 3spd-like core molecular orbitals were constrained to be doubly occupied in all configurations (i.e., the frozen core approximation was used). In addition, the C, N, O, F, Cl, and Br 1s core-counterpart virtual molecular orbital was deleted from the TZ2P basis coupled-cluster calculations.

In order to determine accurate isomeric energy differences and heats of formation, reaction energies have been evaluated at the MP2, CCSD, and CCSD(T) levels of theory using very large atomic natural orbital (ANO) basis sets.[35] The ANO basis set for Br was recently developed by Bauschlicher,[36] while the ANO basis sets for the other atoms have been described in detail previously.[35,37] The basis set denoted ANO1 consists of 6s5p3d, 5s4p2d, 4s3p2d, and 4s2p ANOs on Br, Cl, (C, N, O, and F), and H, respectively, while the ANO2 basis set is composed of 6s5p3d1f, 5s4p2d1f, 4s3p2d1f, and 4s2p1d ANOs on Br, Cl, (C, N, O, and F), and H. The ANO3 basis set consists of 7s6p4d2f, 6s5p3d2f, 5s4p3d2f, and 4s3p2d ANOs on Br, Cl, (C, N, O, and F), and H, respectively, while the ANO4 basis set is composed of 7s6p4d2f1g, 6s5p3d2f1g, 5s4p3d2f1g, and 4s3p2d1f ANOs on Br, Cl, (C, N, O, and F), and H. For the ANO basis sets, only the spherical harmonic components of the d-, f-, and g-type functions were included.

The coupled-cluster geometry optimizations were performed with the TITAN[38] program system. The MP2 and coupled-cluster single-point energies were performed with the TITAN coupled-cluster programs interfaced to the SEWARD[39] integral program, and the SWEDEN[40] self-consistent field and transformation programs. All calculations were performed on either the Computational Chemistry Branch's IBM RS6000 590 computers or the NASA Ames Central Computer Facility's Cray C90.

Results and Discussion

A. Equilibrium Structures and Dipole Moments. The CCSD(T)/TZ2P equilibrium structures, rotational constants, dipole moments, and $\mathcal{T}_1$ diagnostics[41] are presented in Table 1. Experimental data for HOBr, BrNO, and BrCN are also given for comparison. The $\mathcal{T}_1$ diagnostic values for the species with normal neutral Lewis dot structures (i.e., HOBr, FOBr, BrNO, Br_2O, BrCN, and ClOBr) are all less than 0.020 except for BrNO, which has a value of 0.023. The electronic structure of nitrosyl halides is somewhat more difficult to describe (e.g., see ref 4, and references therein), but a $\mathcal{T}_1$ value of 0.023 is still not very large. The two molecules possessing normal Lewis dot structures, but where this electron configuration has partial charges on two atoms ($Br-N^+-C^-$ and $Br-O^+-N^-$), have larger $\mathcal{T}_1$ diagnostic values than their respective isomers possessing normal neutral Lewis dot structures, especially BrON. It is noteworthy that for BrNC and BrON, the electron configuration having a normal charged Lewis dot structure does not seem to be the dominant configuration, at least based on Mulliken population analyses presented later. The $\mathcal{T}_1$ diagnostic values of the hypervalent species (HBrO, FBrO, BrBrO, ClBrO, and BrClO) are all significantly larger than the value obtained for the respective isomers possessing normal neutral Lewis dot structures. This is to be expected since it is known that the electronic structure of hypervalent species is more difficult to describe properly, but the important point is that the $\mathcal{T}_1$ diagnostic values of all the bromine species included in this study are well within the range where the CCSD(T) method is known to yield reliable geometries, vibrational frequencies, dipole moments, and other properties (e.g., see ref 17, and references therein).

As indicated previously, experimental geometries are known only for HOBr, BrNO, and BrCN, and these are all vibrationally averaged structures of one sort or another. Nonetheless, the agreement between the CCSD(T)/TZ2P equilibrium structures and the experimental vibrationally averaged structures is generally good, with the *ab initio* bond distances being too long. The agreement for the HOBr and BrNO bond angles is excellent. In all cases, the Br−X bond distance exhibits the largest difference between theory and experiment, which is largest for the Br−N bond in BrNO (0.033 Å). There is little experience on which to judge the error in the CCSD(T)/TZ2P values for Br−X bond distances, but the differences for the O−H, N−O, and C−N bond distances are all as expected based on the correlation treatment and one-particle basis set that was used (see ref 17 and references therein for examples; note that these errors will decrease as better one-particle basis sets are used with the CCSD(T) method). Our previous studies[1−5] on Cl−X bond distances, however, also showed similar behavior (i.e., that the difference between CCSD(T)/TZ2P and experiment is somewhat larger for Cl−X bonds than found for bonds between first row atoms) and therefore it is expected that the errors for the CCSD(T)/TZ2P Br−O, Br−N and Br−C bonds in Table 1 are typical. In fact, the errors in CCSD(T)/TZ2P Cl−O, Cl−N, and Cl−C bonds are quite similar to those observed here for the analogous bromine bonds. Based on these comparisons, the theoretically predicted structures contained in Table 1 should greatly aid in the analysis of future experiments. It should be borne in mind, however, that also based on earlier studies of

TABLE 1: Total Energies (E_h), Equilibrium Structures, Rotational Constants (MHz), and Dipole Moments (D) of Some Triatomic Molecules Containing Bromine[a]

molecule	parameter	CCSD(T)	expt[b]	molecule	parameter	CCSD(T)
HOBr	E	0.220646		HBrO	E	0.122600
	$\mathcal{T}_1$[c]	0.012			$\mathcal{T}_1$[c]	0.023
	μ	1.49	1.38		μ	4.00
	r_{HO}	0.964	0.961		r_{HBr}	1.458
	r_{OBr}	1.853	1.834		r_{BrO}	1.731
	∠HOBr	102.3	102.3		∠HBrO	106.1
	A_e	609990	613677		A_e	261720
	B_e	10364	10577		B_e	12526
	C_e	10191	10383		C_e	11954
FOBr	E	0.208952		FBrO	E	0.216515
	$\mathcal{T}_1$[c]	0.018			$\mathcal{T}_1$[c]	0.029
	μ	1.58			μ	2.68
	r_{FO}	1.464			r_{FBr}	1.841
	r_{OBr}	1.846			r_{BrO}	1.661
	∠FOBr	106.3			∠FBrO	109.0
	A_e	44695			A_e	20859
	B_e	4036			B_e	6951
	C_e	3702			C_e	5214
BrNO	E	0.249567		BrON	E	0.213607
	$\mathcal{T}_1$[c]	0.023			$\mathcal{T}_1$[c]	0.036
	μ	2.06	1.80		μ	2.78
	r_{BrN}	2.173	2.140		r_{BrO}	2.476
	r_{NO}	1.142	1.146		r_{ON}	1.135
	∠BrNO	114.4	114.5		∠BrON	122.3
	A_e	84326	85500		A_e	96099
	B_e	3658	3747		B_e	2901
	C_e	3506	3586		C_e	2816
Br_2O	E	0.130795		BrBrO	E	0.105184
	$\mathcal{T}_1$[c]	0.017			$\mathcal{T}_1$[c]	0.036
	μ	1.00			μ	2.12
	r_{BrO}	1.865	1.843		r_{BrBr}	2.510
	r_{BrO}	1.865	1.843		r_{BrO}	1.690
	∠BrOBr	112.9	112.2		∠BrBrO	113.1
	A_e	32731			A_e	17881
	B_e	1325			B_e	1637
	C_e	1274			C_e	1500
BrCN	E	0.209868		BrNC	E	0.148722
	$\mathcal{T}_1$[c]	0.015			$\mathcal{T}_1$[c]	0.020
	μ	3.13	2.94		μ	3.09
	r_{BrC}	1.810	1.789		r_{BrN}	1.800
	r_{CN}	1.165	1.158		r_{NC}	1.183
	∠BrCN	180	180		∠BrNC	180
	A_e	4045	4120		A_e	4332
ClOBr	E	0.243764		ClBrO	E	0.221908
	$\mathcal{T}_1$[c]	0.016			$\mathcal{T}_1$[c]	0.034
	μ	0.94			μ	2.26
	r_{ClO}	1.730			r_{ClBr}	2.322
	r_{BrO}	1.868			r_{BrO}	1.682
	∠ClOBr	111.7			∠ClBrO	112.1
	A_e	36563			A_e	18491
	B_e	2281			B_e	3106
	C_e	2147			C_e	2659
BrClO	E	0.210970				
	$\mathcal{T}_1$[c]	0.035				
	μ	1.59				
	r_{BrCl}	2.429				
	r_{ClO}	1.557				
	∠BrClO	115.1				
	A_e	29245				
	B_e	2192				
	C_e	2039				

[a] The energy is reported as $-(E + 2648)$ for HOBr and HBrO, $-(E + 2747)$ for FOBr and FBrO, $-(E + 2702)$ for BrNO and BrON, $-(E + 5220)$ for Br_2O and BrBrO, $-(E + 2665)$ for BrCN and BrNC, and $-(E + 3107)$ for ClOBr, ClBrO, and BrClO. Obtained with the TZ2P basis set. Bond lengths in angstroms and angles in degrees. Rotational constants are for the ^{79}Br isotope. [b] HOBr: substitution structure, dipole moment, and vibrationally averaged rotational constants from ref 18. BrNO: vibrationally averaged structure from ref 10, dipole moment from refs 11 and 12, and vibrationally averaged rotational constants from ref 11. BrCN: vibrationally averaged structure and dipole moment from ref 19, vibrationally averaged rotational constant from ref 20. Br_2O: vibrationally averaged structure from ref 45. [c] See refs 17 and 41 for a detailed discussion of the $\mathcal{T}_1$ diagnostic.

chlorine species,[1-5] it is expected that errors in the bond distances will be somewhat larger for hypervalent compounds than found for the molecules possessing normal Lewis dot structures. This is due to the fact that hypervalent species require larger one-particle basis sets to approach completeness relative to normal valent molecules.

Agreement between CCSD(T)/TZ2P and experiment for the dipole moments of HOBr, BrNO, and BrCN is modest with the *ab initio* values being too high by between 0.11–0.26 D. The largest discrepancy exists for BrNO, but a close examination of the experimental determination shows that this value was guessed in a simulated spectrum. It thus seems likely that the true BrNO μ value is somewhat larger than 1.80 D, and further experimental work is needed. It is likely that the CCSD(T)/TZ2P dipole moments are somewhat too high, as evidenced by the comparisons with experiment for HOBr and BrCN. This is due to one-particle basis set deficiencies and not to an inadequate treatment of electron correlation. Note that the experimental dipole moment for BrCN (3.13 D) is in very good agreement with the value obtained by Kellö and Sadlej (3.19 D) from high-level coupled-cluster calculations. Again, where no experimental data exist, the CCSD(T)/TZ2P dipole moments should aid in the analysis and interpretations of future experiments.

It is interesting that all of the bromine triatomics studied here have rather sizable dipole moments—the largest is 4.00 D for HBrO and the smallest is 0.94 D for ClOBr. The dipole moment of the hypervalent species is always significantly larger than that determined for the analogous normal valent isomer, which is no doubt a reflection of the increased ionic character of the bonding (this is discussed in more detail later).

B. Vibrational Frequencies and Quadratic Force Constants. CCSD(T)/TZ2P harmonic vibrational frequencies and IR intensities are presented in Table 2. Experimental data are given for comparison. Except for BrNO, the experimental data refer to fundamental vibrational frequencies and in some cases these are from matrix isolation experiments rather than gas-phase values. All vibrational data refer to the ^{79}Br isotope. Shifts relative to the ^{81}Br isotope are small, usually less than 1 cm^{-1}. Of the vibrational modes included in Table 2, only the H–O stretch (str) and the H–Br str will have anharmonicities likely to be larger than 50 cm^{-1}. That is, the H–O str anharmonicity is probably near 180 cm^{-1} while the value for the H–Br str is less certain, but likely to be larger than 50 cm^{-1}. Taking into account the anharmonicity of the H–O str, then, the agreement between theory and experiment is very good for all modes which have been observed experimentally. This is true even for the BrBrO, ClBrO, and BrClO hypervalent molecules. This good agreement for vibrational frequencies bolsters confidence in the reliability of the CCSD(T)/TZ2P predicted band centers where no experimental observations have been reported, and also in the reliability of the CCSD(T)/TZ2P equilibrium structures.

In the study[27] where the Cl–O str of BrClO and the Br–O str of ClBrO were observed, no bands from the ClOBr isomer were evident. This is in spite of the fact that ClOBr is the lowest energy isomer (see later discussion). The CCSD(T)/TZ2P IR intensities given in Table 2 indicate that all of the fundamentals of ClOBr have rather small absorbances, and this explains why the ClOBr isomer was not observed. With regard to the IR intensities, another noteworthy result is that the N–O str in both BrNO and BrON has a very large IR intensity. It is hoped that the *ab initio* predictions in Table 2 will aid in future IR studies of bromine molecules.

TABLE 2: Harmonic Frequencies (cm^{-1}) and IR Intensities (km/mol)[a]

molecule/mode	CCSD(T)	expt[b]	molecule/mode	CCSD(T)	expt[b]
HOBr			HBrO		
$\omega_1(a')$ H−O str	3807(73)	3610	$\omega_1(a')$ H−Br str	2292 (40)	
$\omega_2(a')$ bend	1197(39)	1163	$\omega_2(a')$ bend	818(1)	
$\omega_3(a')$ O−Br str	608(7)	620	$\omega_3(a')$ Br−O str	665(22)	
FOBr			FBrO		
$\omega_1(a')$ F−O str	794 (33)		$\omega_1(a')$ Br−O str	855(25)	
$\omega_2(a')$ Br−O str	605 (4)		$\omega_2(a')$ F−Br str	515(85)	
$\omega_3(a')$ bend	297(1)		$\omega_3(a')$ bend	223(9)	
BrNO			BrON		
$\omega_1(a')$ N−O str	1798(741)	1832	$\omega_1(a')$ N−O str	1827(1057)	
$\omega_2(a')$ bend	545(57)	548	$\omega_2(a')$ bend	348(2)	
$\omega_3(a')$ Br−N str	268(34)	270	$\omega_3(a')$ Br−O str	165(7)	
Br_2O			BrBrO		
$\omega_1(a_1)$ sym Br−O str	513(2)	526	$\omega_1(a')$ Br−O str	793(20)	804
$\omega_2(a_1)$ bend	180(0.2)	180	$\omega_2(a')$ Br−Br str	215(16)	236
$\omega_3(b_2)$ asym Br−O str	613(0.1)	623	$\omega_3(a')$ bend	153(3)	
BrCN			BrNC		
$\omega_1(\sigma)$ C−N str	2218(6)	2198	$\omega_1(\sigma)$ C−N str	2089(124)	2067
$\omega_2(\sigma)$ Br−C str	577(1)	575	$\omega_2(\sigma)$ Br−N str	561(0.2)	
$\omega_3(\pi)$ bend	349(4)	342	$\omega_3(\pi)$ bend	194(0.2)	
ClOBr			ClBrO		
$\omega_1(a')$ Cl−O str	658(1)		$\omega_1(a')$ Br−O str	808(25)	819
$\omega_2(a')$ Br−O str	552(1)		$\omega_2(a')$ Cl−Br str	301(34)	
$\omega_3(a')$ bend	233(0.2)		$\omega_3(a')$ bend	182(4)	
BrClO					
$\omega_1(a')$ Cl−O str	893(25)	941			
$\omega_2(a')$[c]	262(15)				
$\omega_3(a')$[c]	164(3)				

[a] IR absorption intensities in parentheses. All vibrational frequencies refer to the ^{79}Br isotope. [b] HOBr: fundamental frequencies from ref 21. BrNO: harmonic frequencies from ref 8. Br_2O: stretching fundamental frequencies from ref 21 (matrix); bending fundamental from ref 45. BrBrO: fundamental frequencies from ref 21 (matrix). BrCN: fundamental frequencies from ref 20. BrNC: fundamental frequency from ref 21 (matrix). ClBrO and BrClO: fundamental frequencies from ref 27. [c] A potential energy distribution analysis shows that there is substantial mixing between the Br−Cl stretching and the BrClO bending motions.

Given the excellent agreement between experiment and theory for the vibrational frequencies, the CCSD(T)/TZ2P quadratic force fields are probably the most accurate available, and therefore these are presented in Table 3. The force constants should be useful in constructing force fields for larger bromine molecules. Units and internal coordinate definitions are given in a footnote to Table 3. Empirically derived force fields for BrNO and BrCN are given for comparison. The agreement between the CCSD(T)/TZ2P and empirical quadratic force fields is generally good.

After submission of this manuscript, we became aware of a very recent experimental determination of the structure and quadratic force constants of Br_2O and the quadratic force constants of HOBr (see ref 45). For comparison, these new data have been included in Tables 1−3. The agreement between the CCSD(T)/TZ2P results and the experimental determinations is very good.

C. Bonding, Isomerization Energies, and Heats of Formation. Mulliken populations of the various bromine triatomics are presented in Table 4. These are based on the CCSD(T) effective one-particle density matrics. As expected, the hypervalent species exhibit a larger degree of ionic bonding as evidenced by larger atomic charges relative to the isomers with normal neutral Lewis dot structures. The ClOBr, ClBrO, and BrClO isomers provide a nice example of how hypervalent bonding involving Br is more pronounced than that involving Cl. That is, for ClBrO the Br is more positive than the Cl in BrClO, and the Cl partial charge is more negative in the former relative to the Br partial charge in the latter. Consistent with this, the Br partial charge in ClOBr is more positive than the Cl partial charge. It was pointed out in an earlier study on Cl hypervalent bonding[3] that the more electronegative the atom or moiety bonded to the hypervalent Cl atom, the more stable the hypervalent compound was relative to the normal valent isomer. Based on this conclusion and the above observations comparing Cl and Br partial charges, it is expected that Br hypervalent compounds will be more stable relative to the normal valent isomer as compared to their Cl analogs. Indeed this is found to be the case.

Energies for the following isomerization reactions are given in Table 5.

$$\mathrm{HOBr} \rightarrow \mathrm{HBrO} + \Delta E_1 \tag{1}$$

$$\mathrm{FOBr} \rightarrow \mathrm{FBrO} + \Delta E_2 \tag{2}$$

$$\mathrm{ClOBr} \rightarrow \mathrm{ClBrO} + \Delta E_3 \tag{3}$$

$$\mathrm{Br_2O} \rightarrow \mathrm{BrBrO} + \Delta E_4 \tag{4}$$

$$\mathrm{ClOBr} \rightarrow \mathrm{BrClO} + \Delta E_5 \tag{5}$$

$$\mathrm{BrNO} \rightarrow \mathrm{BrON} + \Delta E_6 \tag{6}$$

$$\mathrm{BrCN} \rightarrow \mathrm{BrNC} + \Delta E_7 \tag{7}$$

Only for reaction 3 are the MP2 energy differences consistently close to the CCSD(T) values (for the ANO2−ANO4 basis sets), but this is probably fortuitous since the CCSD energy differences are a few kcal/mol higher. The contribution of connected triple excitations is found to be small but significant for all of the reactions 1−7. This suggests that the contribution from higher connected excitations should be very small. Examining the CCSD(T) energy differences, it is evident that the isomerization energies have nearly converged with respect to one−particle basis set improvements for all of the reactions. Based on the demonstrated convergence with respect to one- and n-particle basis set effects, it is expected that the CCSD(T)/ANO4 energy

TABLE 3: Quadratic Force Constants Obtained at the CCSD(T)/TZ2P Level of Theory[a]

molecule/ constant	CCSD(T)	expt[b]	molecule/ constant	CCSD(T)	expt[b]
HOBr			HBrO		
f_{11}	8.09259	8.085	f_{11}	3.07313	
f_{12}	−0.15490	−0.168	f_{12}	0.31116	
f_{13}	0.04760	0.103	f_{13}	−0.15029	
f_{22}	3.14651	3.363	f_{22}	3.60873	
f_{23}	0.39706	0.361	f_{23}	0.20626	
f_{33}	0.74914	0.738	f_{33}	0.78771	
FOBr			FBrO		
f_{11}	3.36303		f_{11}	2.36098	
f_{12}	0.55998		f_{12}	−0.05335	
f_{13}	0.26680		f_{13}	−0.10933	
f_{22}	2.68299		f_{22}	5.68835	
f_{23}	0.19799		f_{23}	−0.09264	
f_{33}	1.16227		f_{33}	0.63776	
BrNO			BrON		
f_{11}	14.60562	15.25 ± 0.04	f_{11}	14.53247	
f_{12}	0.98918	1.47 ± 0.36	f_{12}	−0.19092	
f_{13}	0.21151	0.11 ± 0.20	f_{13}	−0.03764	
f_{22}	1.07106	1.13 ± 0.05	f_{22}	0.40928	
f_{23}	0.09742	0.10 ± 0.02	f_{23}	−0.00182	
f_{33}	1.09265	1.13 ± 0.02	f_{33}	0.43839	
Br_2O			BrBrO		
f_{11}	2.53940	2.812	f_{11}	0.93948	
f_{12}	0.31766	0.366	f_{12}	−0.12918	
f_{13}	0.26614	0.311	f_{13}	−0.02792	
f_{22}	2.53940	2.812	f_{22}	4.89345	
f_{23}	0.26614	0.311	f_{23}	−0.05736	
f_{33}	1.08278	1.026	f_{33}	0.53196	
BrCN			BrNC		
f_{11}	4.11647	4.390	f_{11}	3.87546	
f_{12}	0.03187	−0.221	f_{12}	−0.17974	
f_{22}	17.48602	17.194	f_{22}	15.54058	
f_{33}	0.32311	0.304	f_{33}	0.10855	
ClOBr			ClBrO		
f_{11}	2.80619		f_{11}	1.24853	
f_{12}	0.37960		f_{12}	−0.08730	
f_{13}	0.29498		f_{13}	−0.04480	
f_{22}	2.48549		f_{22}	5.08879	
f_{23}	0.24138		f_{23}	−0.06486	
f_{33}	1.14917		f_{33}	0.58580	
BrClO					
f_{11}	0.71243				
f_{12}	−0.24094				
f_{13}	−0.01511				
f_{22}	5.05397				
f_{23}	−0.03322				
f_{33}	0.56611				

[a] Units are aJ/Å^2, aJ/(Å·rad), and aJ/rad^2. Definition of the internal coordinates (including order) is as follows; HOBr: r_{HO}, r_{BrO}, ∠HOBr; HBrO: r_{HBr}, r_{BrO}, ∠HBrO; FOBr: r_{FO}, r_{BrO}, ∠FOBr; FBrO: r_{FBr}, r_{BrO}, ∠FBrO; BrNO: r_{NO}, r_{BrN}, ∠BrNO; BrON: r_{NO}, r_{BrO}, ∠BrON; Br_2O: r_{BrO}, r_{BrO}, ∠BrOBr; BrBrO: r_{BrBr}, r_{BrO}, ∠BrBrO; BrCN: r_{BrC}, r_{CN}, (180 − ∠BrCN); BrNC: r_{BrN}, r_{CN}, (180 − ∠BrNC); ClOBr: r_{ClO}, r_{BrO}, ∠ClOBr; ClBrO: r_{ClBr}, r_{BrO}, ∠ClBrO; BrClO: r_{BrCl}, r_{ClO}, ∠BrClO. [b] BrNO: ref 8. BrCN: ref 20. HOBr and Br_2O: ref 45.

TABLE 4: Atomic Charge Distribution Based on Mulliken Population Analyses[a]

	HOBr	HBrO	ClOBr	ClBrO	BrClO
H/Cl	+0.33	+0.02	+0.14	−0.15	+0.50
O	−0.52	−0.62	−0.39	−0.52	−0.43
Br	+0.19	+0.60	+0.25	+0.68	−0.07

	FOBr	FBrO	Br_2O	BrBrO[b]
F/Br	−0.12	−0.39	+0.24	−0.09
O	−0.16	−0.55	−0.48	−0.51
Br	+0.29	+0.94	+0.24	+0.60

	BrNO	BrON	BrCN	BrNC
O/C	−0.14	−0.06	−0.28	+0.12
N	+0.33	+0.42	−0.14	−0.49
Br	−0.19	−0.36	+0.42	+0.37

[a] Based on the CCSD(T)/TZ2P effective one-particle density matrices. [b] The third row refers to the central Br atom.

TABLE 5: Isomerization Energies (kcal/mol)[a]

	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	ΔE_6	ΔE_7
MP2/ANO1	64.3	−11.9	14.7	19.7	21.8	19.9	41.9
MP2/ANO2	61.7	−15.5	12.6	17.7	20.4	21.3	41.4
MP2/ANO3	60.4	−17.3	11.7	17.0	19.7	21.5	41.3
MP2/ANO4	60.5	−17.4	11.5	16.7	19.5	21.6	41.3
CCSD/ANO1	62.7	−4.0	17.8	20.8	25.0	27.3	37.1
CCSD/ANO2	60.7	−7.0	16.1	19.5	24.2	28.7	36.7
CCSD/ANO3	59.7	−8.5	15.6	19.1	24.0	29.0	36.6
CCSD/ANO4	60.2	−8.5	15.5	19.0	23.9	29.2	36.7
CCSD(T)/TZ2P	61.5	−4.7	13.7	16.1	20.6	22.6	38.4
CCSD(T)/ANO1	61.6	−6.3	13.9	16.6	19.5	21.9	37.3
CCSD(T)/ANO2	59.7	−9.2	12.3	15.2	18.7	23.1	36.9
CCSD(T)/ANO3	58.4	−10.9	11.6	14.8	18.4	23.6	36.8
CCSD(T)/ANO4	58.9	−11.0	11.5	14.6	18.2	24.1	36.8
ΔZPVE[b]	−2.6	−0.1	−0.2	−0.2	−0.2	−0.4	−0.7
ΔVT[c]	0.0	0.1	0.2	0.2	0.2	0.2	0.3

[a] See eqs 1−7 for definition of the ΔE quantities. Energies determined at CCSD(T)/TZ2P equilibrium geometries. Zero-point vibrational energies not included—see text for energy differences where these are included. [b] Zero-point vibrational energies determined using CCSD(T)/TZ2P harmonic frequencies. [c] Energy changes due to thermal population of vibrational energy levels at 298.15 K.

differences should be accurate to better than ±0.8 kcal/mol. Adding the difference in zero-point vibrational energies (ZPVE) to the CCSD(T)/ANO4 value, we obtain 56.3, −11.1, 11.3, 14.4, 18.0, 23.7, and 35.9 kcal/mol for reactions 1−7, respectively. This is the reaction enthalpy at 0 K; for later purposes the change in the reaction enthalpies due to thermal population of vibrational energy levels at 298.15 K is also presented in Table 5. It is thus apparent that the isomers having a normal neutral Lewis dot structure are the lowest energy species in every case except for FOBr/FBrO. This is similar to the situation for the Cl analogs (see refs 1−5 and references therein), but as indicated previously, bromine hypervalent isomers are more stable than their chlorine analogs. Again the ClOBr, ClBrO, and BrClO isomers provide a useful example. While ClOBr is the lowest energy isomer, comparison of reaction energies ΔE_3 and ΔE_5 (above) shows that ClBrO is about 6.7 kcal/mol more stable than BrClO. Further, comparison of the isomerization energies of the analogous Cl compounds supports this assertion (e.g., FClO is predicted[3] to be more stable than FOCl by only 6.0 kcal/mol rather than the 11.1 kcal/mol found for FBrO/FOBr).

Comparison of ΔE_2 through ΔE_4 shows that for XBrO compounds, the more electronegative the X species the more stable the hypervalent compounds, similar to chlorine hypervalent compounds. The accurate isomerization energies determined from the data in Table 5 should be useful in assessing the stratospheric significance of bromine compounds as well as determining accurate heats of formation. However, in order to evaluate accurate heats of formation from this data it is first necessary to place some of these bromine compounds on an absolute scale. That is, it is necessary to determine accurate heats of formation for a few bromine compounds first. In previous studies on fluorine and chlorine compounds, our approach has been to compute accurate isodesmic and/or homodesmic reaction energies and then use these together with accurate experimental heats of formation of some compounds in order to determine heats of formation of new compounds. This approach has the advantage that the energy differences determined from the *ab initio* calculations involve a high degree of cancellation of errors, and therefore it is relatively easy to approach one- and *n*-particle space convergence (note that the cancellation of errors is certainly better for isodesmic compared to homodesmic reactions, but with CCSD(T) and large ANO basis sets residual errors are generally small even for homodesmic reactions). In the case of chlorine and especially bromine, there is also the big advantage that since only closed-shell molecules are used in the isodesmic and homodesmic reactions, it is not necessary to include explicitly spin–orbit effects. The difficulty with this approach is that it requires knowledge of an accurate experimental heat of formation for at least one closed-shell bromine. As indicated previously, there is some debate currently[22–24] concerning the heat of formation of HOBr, with estimates ranging from −9 to −19 kcal/mol (298 K), although the more recent determinations range from −9 to −14 kcal/mol. This range is still quite large, but probably the $\Delta H^\circ_{f,298}$ ($\Delta H^\circ_{f,0}$) value determined by Ruscic and Berkowitz,[23] −13.4 ± 0.4 kcal/mol (−10.9 ± 0.4 kcal/mol; these are actually lower bounds), is the most reliable since the auxiliary thermochemical data used in this study is the most reliable (relative to that used in refs 22 and 24). According to ref 14, the heat of formation of BrNO is 19.6 ± 0.2 kcal/mol (298 K), which has been obtained from experiments carried out in the 1920s and 1930s. This is a very small uncertainty, although there are many examples in which the heats of formation of similar fluorine and chlorine compounds were thought to possess very small uncertainties and this was incorrect (e.g., see refs 42 and 43). We may examine the consistency of the HOBr and BrNO experimental heats of formation and also determine heats of formation for the other bromine compounds included in this study by computing the reaction energies of the following homodesmic (reactions 8 and 12) and isodesmic (reactions 9–11) reactions, and these are presented in Table 6.

$$\mathrm{BrNO} + \mathrm{H_2O} \rightarrow \mathrm{HNO} + \mathrm{HOBr} + \Delta E_8 \qquad (8)$$

$$\mathrm{HOBr} + \mathrm{HOBr} \rightarrow \mathrm{H_2O} + \mathrm{Br_2O} + \Delta E_9 \qquad (9)$$

$$\mathrm{Br_2O} + \mathrm{HOF} \rightarrow \mathrm{HOBr} + \mathrm{FOBr} + \Delta E_{10} \qquad (10)$$

$$\mathrm{HOBr} + \mathrm{HOCl} \rightarrow \mathrm{ClOBr} + \mathrm{H_2O} + \Delta E_{11} \qquad (11)$$

$$\mathrm{BrCN} + \mathrm{HOCl} \rightarrow \mathrm{ClCN} + \mathrm{HOBr} + \Delta E_{12} \qquad (12)$$

TABLE 6: Homodesmic and isodesmic reaction energies (kcal/mol)[a]

	ΔE_8	ΔE_9	ΔE_{10}	ΔE_{11}	ΔE_{12}
MP2/ANO1	53.3	−3.5	−0.9	−3.2	−8.5
MP2/ANO2	50.8	−3.4	−0.9	−3.1	−9.0
MP2/ANO3	51.2	−3.4	−1.2	−3.2	−9.0
MP2/ANO4	51.1	−3.4	−1.1	−3.2	−9.2
CCSD/ANO1	45.5	−0.9	−2.0	−1.0	−7.6
CCSD/ANO2	42.8	−0.7	−2.0	−0.8	−8.2
CCSD/ANO3	43.2	−0.7	−2.4	−0.7	−8.1
CCSD/ANO4	43.2	−0.6	−2.3	−0.6	−8.4
CCSD(T)/TZ2P	49.3	−1.2	−2.8	−1.3	−6.4
CCSD(T)/ANO1	49.2	−1.8	−2.3	−1.9	−7.5
CCSD(T)/ANO2	46.8	−1.7	−2.2	−1.8	−8.1
CCSD(T)/ANO3	47.1	−1.7	−2.6	−1.7	−8.0
CCSD(T)/ANO4	47.1	−1.6	−2.5	−1.7	−8.3
ΔZPVE[b]	−0.6	−0.7	−0.1	−0.7	0.1
ΔVT[c]	−0.3	0.4	−0.1	0.4	0.0

[a] See eqs 8–12 for definition of the ΔE quantities. Zero-point vibrational energies not included—see text for energy differences where these are included. [b] Zero-point vibrational energies determined using CCSD(T)/TZ2P harmonic frequencies. [c] Energy changes due to thermal population of vibrational energy levels at 298.15 K.

TABLE 7: Heats of Formation (kcal/mol)[a]

	$\Delta H^\circ_{f,0}$	$\Delta H^\circ_{f,298.15}$
HBrO	+45.4	+42.9
FOBr	+21.4	+19.2
FBrO	+10.3	+8.2
ClOBr	+26.7	+24.6
ClBrO	+38.0	+36.1
BrClO	+44.7	+42.8
$\mathrm{Br_2O}$	+33.0	+29.1
BrBrO	+47.4	+43.7
BrNO	+26.4	+24.2
BrON	+50.1	+48.1
BrCN	+47.2	+45.6
BrNC	+83.3	+82.0

[a] Based on the data in Tables 5 and 6 together with some experimental and theoretical heats of formation—see text.

A quick examination of the results in Table 6 shows that the reaction energies ΔE_8 through ΔE_{12} are very nearly converged with respect to one- and *n*-particle basis set improvements. Therefore, taking the CCSD(T)/ANO4 ΔE values as our best computed result and correcting these with the contribution from zero-point energies, we obtain 46.5, −2.3, −2.6, −2.4, and −8.3 kcal/mol as the best estimates for ΔE_8 through ΔE_{12}, respectively (0 K). Based on the exhibited convergence and the established reliability of the CCSD(T) method, these values are expected to be accurate to better than ±1.0 kcal/mol. Combining ΔE_8 with experimental heats of formation for BrNO and H_2O,[14] and a new determination[44] for the heat of formation of HNO (26.7 and 26.0 kcal/mol for $\Delta H^\circ_{f,0}$ and $\Delta H^\circ_{f,298}$, respectively), the heat of formation of HOBr is computed to be −15.5 kcal/mol (0 K) or −18.0 kcal/mol (298 K). The $\Delta H^\circ_{f,298}$ value is not in very good agreement with the determination of Ruscic and Berkowitz, being 4.6 kcal/mol lower. This is especially bad agreement considering that the Ruscic and Berkowitz value is a lower bound. Hence it is reasonable to conclude that the experimental $\Delta H^\circ_{f,298}$ value for BrNO is in error and instead we use the experimental heats of formation of HOBr[23] and H_2O,[14] the recent determination for HNO,[44] and the best estimate for ΔE_8 to arrive at a new $\Delta H^\circ_{f,298}$ value for BrNO, 26.4 kcal/mol. It is difficult to assign an uncertainty to the present computed heat of formation—the estimated uncertainties of all of the individual contributing components are rather small, and since these are unrelated the overall uncertainty should be less than their sum. We believe that the uncertainties assigned to the computed reaction energies are conservative, so if the $\Delta H^\circ_{f,298}$ value for BrNO determined in this work is in error by several kcal/mol, then the largest error will probably arise from the experimental heat of formation of HOBr.

In any case, assuming that the experimental heat of formation for HOBr[23] and the computed heat of formation for BrNO are accurate, the data contained in Tables 5 and 6, together with experimental heats of formation for H_2O, HOF,[43] HOCl,[14] and ClCN,[14] may be used to determine heats of formation for the remaining bromine compounds included in this work. These are collected in Table 7. It is noteworthy that Orlando and Burkholder[24] were able to deduce that $\Delta H_f(\mathrm{Br_2O}) - 2\Delta H_f(\mathrm{HOBr}) = 55.5$ kcal/mol (assuming that $\Delta S \approx 0$) based on an equilibrium between HOBr, Br_2O, and H_2O being reached. In the present work we obtain 55.9 kcal/mol for this quantity (from reaction 9 and the experimental $\Delta H^\circ_{f,298}(\mathrm{H_2O})$ value), which strongly supports the accuracy of the present *ab initio* calculations. Should an unquestionably accurate experimental heat of formation of any of the bromine triatomics included in this study be obtained, the heats of formation of all of the other bromine triatomics may be derived from the data in Tables 5 and 6 together with the previously noted experimental heats of formation of H_2O, HOF, HOCl, and ClCN and the new theoretical heat of formation of HNO.[44]

Conclusions

The CCSD(T)/TZ2P level of theory has been used to determine accurate equilibrium geometries, harmonic frequencies, dipole moments, and quadratic force fields for HOBr, HBrO, FOBr, FBrO, ClOBr, ClBrO, BrClO, Br_2O, BrBrO, BrNO, BrON, BrCN, and BrNC. The CCSD(T)/TZ2P geometries and vibrational frequencies are in very good agreement with the available experimental data, although the CCSD(T) dipole moment values are consistently smaller than experiment. This is most likely due to errors in both the theoretical treatment (i.e., one-particle basis set deficiencies) and the experimental analyses. An explanation is provided for the fact that ClOBr was not observed in matrix isolation experiments in which ClBrO and BrClO were both detected. That is, the IR intensities of the stretching modes in ClOBr are very small. It is expected that the *ab initio* structures, vibrational frequencies, and quadratic force fields should be useful in the analysis of future experimental studies.

Accurate isomerization energies are computed at the CCSD(T) level of theory using large ANO basis sets that include *g*-type functions. With one exception, the isomer possessing a normal neutral Lewis dot structure is the lowest energy species. In the one exception FBrO is found to be 11.1 kcal/mol lower in energy than FOBr (0 K). Using a set of homodesmic and isodesmic reaction energies, heats of formation of all of the Br triatomics have been computed. The accuracy of the *ab initio* calculations is demonstrated by the excellent agreement with a recent experimental study[24] for the determination of the $\Delta H_f(Br_2O) - 2\Delta H_f(HOBr)$ quantity. The accuracy of the proposed heats of formation, however, ultimately depends on the reliability of the experimental heat of formation of HOBr.

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