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# Ab Initio and Density Functional Studies of $HOBr-H_2O$ and $BrONO_2-H_2O$ Complexes

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Ab initio and density functional investigations of $HOBr-H_2O$ and $BrONO_2-H_2O$ complexes were performed. For $HOBr-H_2O$ complex, structures and vibrational frequencies were determined at MP2 and B3LYP levels of theory with basis sets up to 6-311++G(d,p), and binding energies were obtained from MP4/6-311++G(2df,2pd) single-point energy calculations. Two $C_s$ symmetry conformers were found, and the binding energies including ZPE correction are 5.6 and 5.4 kcal mol$^{-1}$ for the syn and anti conformers, respectively. Electron correlation is important in determining the equilibrium structure of $BrONO_2-H_2O$ complex which has a $C_s$ equilibrium structure at HF/6-311G(d,p) level but slightly deviates from it at B3LYP/6-311G(d,p) level. The bromine atom acts as an electron acceptor in the complex. The ZPE corrected binding energy determined at B3LYP/6-311++G(2df,2p) level is 4.0 kcal mol$^{-1}$.

## Introduction

Bromine compounds are considered to be connected with the ozone depletion in the stratosphere.[1−3] These compounds are minor constituents of the stratosphere, yet they are suggested to have greater ozone destruction potential than chlorine compounds.[4,5] Hypobromous acid (HOBr) and bromine nitrate ($BrONO_2$) are two major bromine reservoir species in the atmosphere. HOBr can be formed in the atmospheric reaction of $HO_2$ with BrO:[2,6]

$$HO_2 + BrO \rightarrow HOBr + O_2 \qquad (1)$$

or by the heterogeneous reaction of $BrONO_2$ on the surface of aerosol particles, as is the case of $ClONO_2$:[7−9]

$$BrONO_2 + H_2O \rightarrow HOBr + HNO_3 \qquad (2)$$

The photolysis of HOBr in the lower atmosphere produces bromine, which leads to an important catalytic cycle for ozone destruction:[1−3]

$$HO_2 + BrO \rightarrow HOBr + O_2 \qquad (1)$$

$$HOBr + h\nu \rightarrow OH + Br \qquad (3)$$

$$Br + O_3 \rightarrow BrO + O_2 \qquad (4)$$

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (5)$$

$$\text{net:} \qquad 2O_3 \rightarrow 3O_2$$

Hydrolysis of halogen nitrate is very slow in the gas phase, but it proceeds readily on cold water−ice surface.[7−9] Therefore, the characterization of the interaction of halogen reservoir species with water which is the most abundant molecules in polar stratospheric cloud (PSC) will be helpful to the understanding of the mechanism of the heterogeneous catalytic reaction for the reservoir species.

HOBr has been extensively studied. Both vibrationally averaged structure[10] and fundamental frequencies[11] have been experimentally deduced or observed. Recent high level ab initio[12] and experimental[13−16] investigations have determined the heat of formation of HOBr. The CCSD/TZ2P geometry and vibrational frequency obtained by Lee[17] are in good agreement with the experimental data.

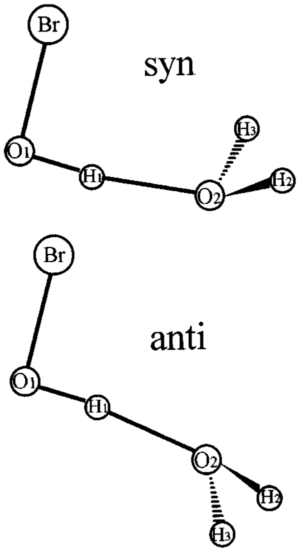

**Figure 1.** Equilibrium structures of the syn and anti conformers of the $HOBr-H_2O$ complex.

The gas-phase structure of $BrONO_2$ was established only 3 years ago from electron diffraction data.[18] The IR spectra of gas-phase and matrix-isolated $BrONO_2$ strongly support a planar structure for $BrONO_2$, similar to the structure of $HONO_2$ and $ClONO_2$.[19] We are aware of only one theoretical study of $BrONO_2$. The equilibrium structure optimized at the Hartree−Fock level with DZP basis reported by Rayez and Destriau[20] does not match the experimental structure well in today's view. Therefore, a higher level theoretical calculation of $BrONO_2$ is required.

In this paper, we report ab initio and density functional studies of the molecular structures, vibrational frequencies of HOBr, $BrONO_2$, $HOBr-H_2O$, and $BrONO_2-H_2O$ and the binding energies of HOBr and $BrONO_2$ with water. Comparisons to the corresponding $HOCl-H_2O$[21] and $ClONO_2-H_2O$[22] complexes will also be made.

## Methods of Calculation

Ab initio and density functional calculations have been performed with the GAUSSIAN 94 programs[23] on a DEC Alpha

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**TABLE 1: Calculated Geometry Parameters for HOBr, $H_2O$, and HOBr−$H_2O$ Complex (Distance *R* in angstroms, Bond Angle α and Dihedral Angle *δ* in degrees)**

| species | parameter | MP2/6-311G(d,p) | MP2/6-311++G(d,p) | B3LYP/6-311G(d,p) | B3LYP/6-311++G(d,p) | expt[a] |
|---|---|---|---|---|---|---|
| HOBr | $R$(OH) | 0.965 | 0.967 | 0.967 | 0.968 | 0.961 |
| | $R$(BrO) | 1.860 | 1.861 | 1.871 | 1.870 | 1.834 |
| | α(BrOH) | 101.2 | 102.2 | 102.3 | 103.2 | 102.3 |
| $H_2O$ | $R$(OH) | 0.958 | 0.960 | 0.962 | 0.962 | 0.957 |
| | α(HOH) | 102.4 | 103.4 | 103.8 | 105.1 | 104.5 |
| syn | $R(BrO_1)$ | 1.852 | 1.852 | 1.866 | 1.865 | |
| | $R(H_1O_1)$ | 0.977 | 0.977 | 0.982 | 0.980 | |
| | $R(O_2H_1)$ | 1.793 | 1.825 | 1.788 | 1.820 | |
| | $R(H_2O_2)$ | 0.960 | 0.961 | 0.963 | 0.963 | |
| | $\alpha(H_1O_1Br)$ | 100.8 | 102.0 | 101.9 | 103.2 | |
| | $\alpha(O_1H_1O_2)$ | 174.0 | 178.1 | 173.9 | 179.5 | |
| | $\alpha(H_2O_2H_3)$ | 103.7 | 104.4 | 105.2 | 106.2 | |
| | $\delta(BrO_1H_1O_2)$ | 0.0 | 0.0 | 0.0 | 0.0 | |
| | $\delta(O_1H_1O_2H_2)$ | 58.8 | 64.8 | 58.7 | 67.4 | |
| anti | $R(BrO_1)$ | 1.852 | 1.853 | 1.866 | 1.865 | |
| | $R(H_1O_1)$ | 0.976 | 0.976 | 0.981 | 0.980 | |
| | $R(O_2H_1)$ | 1.785 | 1.822 | 1.784 | 1.815 | |
| | $R(H_2O_2)$ | 0.959 | 0.961 | 0.963 | 0.963 | |
| | $\alpha(H_1O_1Br)$ | 101.3 | 102.4 | 102.5 | 103.8 | |
| | $\alpha(O_1H_1O_2)$ | 176.5 | 175.7 | 174.2 | 173.1 | |
| | $\alpha(H_2O_2H_3)$ | 104.0 | 104.5 | 105.5 | 106.1 | |
| | $\delta(BrO_1H_1O_2)$ | 180.0 | 180.0 | 180.0 | 180.0 | |
| | $\delta(O_1H_1O_2H_2)$ | 60.9 | 64.8 | 60.1 | 64.7 | |

[a] HOBr from ref 11; $H_2O$ from ref 31.

**TABLE 2: Vibrational Frequencies ($cm^{-1}$) of HOBr, $H_2O$, and HOBr−$H_2O$ Complex**

| species | sym | mode no. | approx assignment | MP2/6-311G(d,p)[a] | MP2/6-311++G(d,p)[a] | B3LYP/6-311G(d,p) | B3LYP/6-311++G(d,p) | expt[b] |
|---|---|---|---|---|---|---|---|---|
| HOBr | A′ | 1 | OH str | 3839 | 3825 | 3786 | 3787 | 3610 |
| | | 2 | bend | 1167 | 1143 | 1173 | 1152 | 1163 |
| | | 3 | BrO str | 619 | 617 | 621 | 621 | 620 |
| $H_2O$ | $B_2$ | 1 | asym OH str | 4011 | 4001 | 3905 | 3922 | 3943 |
| | $A_1$ | 2 | sym OH str | 3904 | 3884 | 3809 | 3817 | 3832 |
| | | 3 | bend | 1668 | 1630 | 1639 | 1603 | 1648 |
| syn | A′ | 1 | $OH_w$ sym str | 3889 | 3873 | 3809 | 3817 | |
| | | 2 | $OH_{Br}$ str | 3626 | 3638 | 3506 | 3549 | |
| | | 3 | $HOH_w$ bend | 1657 | 1643 | 1630 | 1619 | |
| | | 4 | HOBr bend | 1334 | 1279 | 1332 | 1280 | |
| | | 5 | BrO str | 628 | 628 | 615 | 619 | |
| | | 6 | $HOH_w$ rock | 332 | 293 | 323 | 227 | |
| | | 7 | H-bond str | 237 | 211 | 254 | 216 | |
| | | 8 | dimer rock | 78 | 66 | 88 | 75 | |
| | A″ | 9 | $OH_w$ asym str | 3996 | 3986 | 3906 | 3918 | |
| | | 10 | H-bond wag | 768 | 725 | 773 | 727 | |
| | | 11 | torsion | 235 | 234 | 248 | 226 | |
| | | 12 | HOH wag | 51 | 21 | 12 | 10 | |
| anti | A′ | 1 | $OH_w$ sym str | 3893 | 3874 | 3811 | 3813 | |
| | | 2 | $OH_{Br}$ str | 3642 | 3644 | 3525 | 3550 | |
| | | 3 | $HOH_w$ bend | 1653 | 1639 | 1627 | 1620 | |
| | | 4 | HOBr bend | 1329 | 1281 | 1321 | 1281 | |
| | | 5 | BrO str | 631 | 628 | 617 | 616 | |
| | | 6 | $HOH_w$ rock | 295 | 293 | 290 | 269 | |
| | | 7 | H-bond str | 229 | 202 | 230 | 204 | |
| | | 8 | dimer rock | 71 | 62 | 73 | 68 | |
| | A″ | 9 | $OH_w$ asym str | 4002 | 3988 | 3910 | 3914 | |
| | | 10 | H-bond wag | 768 | 745 | 766 | 735 | |
| | | 11 | $H_2O$ wag | 218 | 217 | 224 | 222 | |
| | | 12 | HOH wag | 45 | 53 | 41 | 61 | |

[a] MP2 vibrational frequencies of the HOBr−$H_2O$ complex were calculated by a numerical method. [b] HOBr from ref 12; $H_2O$ from ref 31.

**TABLE 3: MP2/6-311++G(d,p) Vibrational Frequency Shifts ($cm^{-1}$) of $H_2O$ and HOBr upon Complexation**

| species | mode | $\Delta\nu$ syn | $\Delta\nu$ anti | species | mode | $\Delta\nu$ syn | $\Delta\nu$ anti |
|---|---|---|---|---|---|---|---|
| $H_2O$ | asym OH str | −15 | −13 | HOBr | OH str | −187 | −181 |
| | sym OH str | −11 | −10 | | bend | +136 | +138 |
| | bend | +13 | +9 | | BrO str | +11 | +11 |

3000/300 workstation. For HOBr and HOBr−$H_2O$ complex, all equilibrium geometries were optimized at the MP2 (frozen core) level of the theory[24] and with the density functional B3LYP approach, i.e., the Becke's three-parameter nonlocal exchange functional[25] with the nonlocal correlation functional of Lee, Yang, and Parr.[26] Two basis sets have been used for geometry optimization: 6-311G(d,p) and 6-311++G(d,p) which include polarization functions for both heavy atoms and hydrogen, and for the latter, the diffuse functions were also added. Here the 6-311G stands for the 6-311G basis for the first-row atoms, the McLean−Chandler (12s,9p) → (621111,52111) basis sets for the second-row atoms[27] and the 6-311G basis set of McGrath, Curtiss, and co-worker's for bromine.[28,29]

**TABLE 4: Calculated Absolute Energies and Binding Energies of the $HOBr-H_2O$ complex[a]**

| theory level | $H_2O$ | HOBr | syn | anti | Δ syn[b] | Δ anti[b] |
|---|---|---|---|---|---|---|
| MP2/6-311G(d,p) | −76.263 97 | −2648.101 09 | −2724.380 86 | −2724.380 41 | 7.9 | 7.5 |
| MP2/6-311++G(d,p) | −76.274 92 | −2648.109 65 | −2724.397 63 | −2724.397 63 | 6.2 | 6.1 |
| B3LYP/6-311G(d,p) | −76.447 45 | −2649.937 32 | −2726.401 28 | −2726.400 76 | 8.2 | 7.9 |
| B3LYP/6-311++G(d,p) | −76.458 53 | −2649.943 88 | −2726.414 58 | −2726.414 51 | 5.6 | 5.5 |
| MP4/6-311++G(d,p)//B3LYP/6-311++G(d,p) | −76.287 17 | −2648.136 09 | −2724.436 21 | −2724.436 20 | 6.1 | 6.0 |
| MP4/6-311++G(2d,2p)//B3LYP/6-311++G(d,p) | −76.309 17 | −2648.162 78 | −2724.483 87 | −2724.483 69 | 5.5 | 5.3 |
| MP4/6-311++G(2df,2pd)//B3LYP/6-311++G(d,p) | −76.334 09 | −2648.223 29 | −2724.569 52 | −2724.569 29 | 5.6 | 5.4 |

[a] Absolute energies in hartrees. [b] Binding energies in kcal $mol^{-1}$, and ZPE correction is included.

**TABLE 5: Calculated Geometry Parameters for $BrONO_2$ (Distance $R$ in angstroms and Angle α in degrees)**

| parameter | HF/6-311G | HF/6-311G(d) | MP2/6-311G | MP2/6-311G(d) | B3LYP/6-311G | B3LYP/6-311G(d) | expt[a] |
|---|---|---|---|---|---|---|---|
| $R(BrO_1)$ | 1.863 | 1.815 | 1.927 | 1.855 | 1.918 | 1.866 | 1.829 |
| $R(O_1N)$ | 1.377 | 1.360 | 1.657 | 1.515 | 1.529 | 1.483 | 1.456 |
| $R(O_2N)$ | 1.213 | 1.169 | 1.235 | 1.193 | 1.231 | 1.191 | 1.205 |
| $R(O_3N)$ | 1.205 | 1.165 | 1.240 | 1.196 | 1.231 | 1.192 | 1.205 |
| $\alpha(BrO_1N)$ | 118.9 | 117.8 | 111.8 | 113.3 | 115.3 | 115.3 | 113.9 |
| $\alpha(O_1NO_2)$ | 118.6 | 118.5 | 117.5 | 117.9 | 118.3 | 118.3 | 119.5 |
| $\alpha(O_1NO_3)$ | 112.7 | 111.6 | 107.0 | 108.0 | 108.8 | 108.8 | 106.6 |

[a] From ref 19.

**TABLE 6: Fundamental Vibrational Frequencies ($cm^{-1}$) and IR Intensities (km/mol) of $BrONO_2$**

| mode | | approx assignment | MP2/6-311G | MP2/6-311G(d) | B3LYP/6-311G | B3LYP/6-311G(d) | expt[a] |
|---|---|---|---|---|---|---|---|
| A′ | $\nu1$ | $NO_2$ asym str | 1878 | 1951 | 1612 | 1791(320) | 1714(vs) |
| | $\nu_2$ | $NO_2$ sym str | 1163 | 1319 | 1209 | 1341(307) | 1288(vs) |
| | $\nu_3$ | $NO_2$ scissors | 712 | 795 | 754 | 827(218) | 806(vs) |
| | $\nu_4$ | $BrO_1$ str | 655 | 739 | 699 | 739(0.5) | 750(vs) |
| | $\nu_5$ | $O_1NO_2$ ip bend | 398 | 502 | 530 | 563(86) | 572(vs) |
| | $\nu_6$ | $O_1N$ str | 279 | 383 | 362 | 390(1.6) | 394 |
| | $\nu_7$ | $BrO_1N$ bend | 175 | 212 | 187 | 206(0.06) | 245(w) |
| A″ | $\nu8$ | $O_1NO_2$ op bend | 619 | 723 | 665 | 735(14) | 728(mw) |
| | $\nu_9$ | torsion | 97 | 112 | 96 | 107(0.6) | |

[a] From ref 20. $\nu_6$ was deduced from overtone. All the frequencies were measured in the gas phase except $\nu_7$, which was obtained in the solid.

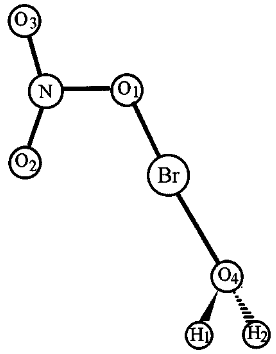

**Figure 2.** Equilibrium structure of the $BrONO_2-H_2O$ complex.

Analytic or numerical MP2 and analytic B3LYP vibrational frequencies were calculated for optimized geometries. Single-point energies were determined at MP4(SDTQ) level with several larger basis sets: 6-311++G(d,p), 6-311++G(2d,2p), and 6-311++G(2df,2pd), and B3LYP frequencies were used for the zero-point energy (ZPE) correction to the binding energy of HOBr with water. It was estimated that the error in the binding energy for the MP4/6-311++G(2df,2pd) calculation was 0.5 kcal $mol^{-1}$.

For $BrONO_2$ and $BrONO_2-H_2O$, the equilibrium structures were optimized at the Hartree−Fock, MP2, or B3LYP levels with 6-311G and 6-311G(d,p) basis sets, and vibrational frequencies were also calculated at corresponding equilibrium structures. Single-point energies were calculated at B3LYP level with 6-311++G(d,p), 6-311++G(2d,p), and 6-311++G-(2df,2p) basis sets. It was difficult to give error bars for B3LYP calculations, but we estimated that the error in the binding energy for the B3LYP/6-311++G(2df, 2p) was less than 1.5 kcal $mol^{-1}$.

## Results and Discussion

**$HOBr-H_2O$ Complex.** The optimized equilibrium structures of the monomers and the complex are listed in Table 1. Results of HOBr and $H_2O$ at these four theory levels are all consistent with the experiment.[10,30] The calculated Br−O bond length is about 0.03 Å longer than the experiment. Lee[17] has obtained a more accurate Br−O bond length using a higher CCSD(T) method indicating that the treatment of electron correlation is important to the prediction of the Br−O bond length.

We have found two conformers of $HOBr-H_2O$ complex, both with $C_s$ symmetry, as depicted in Figure 1. The conformers differ by the orientation of the water molecule with respect to the bromine, which is either syn or anti to the bromine atom. These two structures are similar to that of recent reported $HOCl-H_2O$ complex.[21] However, at the lower Hartree−Fock level of theory, only one syn conformer was found, suggesting the importance of electron correlation. The hydrogen bond length of $HOBr-H_2O$ is about 1.82 Å, a little longer than that of corresponding $HOCl-H_2O$ complex and much smaller than that in water dimer,[31] which basically reflects the sequence of hydrogen bond strength of this series of complexes. Formation of the hydrogen bond causes small changes in HOBr and $H_2O$ molecular geometries. The most significant variation in HOBr is the O−H bond, which is lengthened by 0.009−0.012 Å. The Br−O bond length is shortened by about 0.005 Å. The O−H bond length in $H_2O$ remains almost unaffected, but the H−O−H bond angle increases by 1.0°.

Table 2 shows the approximate assignments and frequencies

**TABLE 7: Calculated Geometry Parameters for $BrONO_2$−$H_2O$ Complex (Distance $R$ in angstroms, Bond Angle $\alpha$ and Dihedral Angle $\delta$ in degrees)**

| parameter | HF/6-311G(d,p) | B3LYP/6-311G(d,p) |
|---|---|---|
| $R$(BrO$_1$) | 1.833 | 1.904 |
| $R$(O$_1$N) | 1.344 | 1.437 |
| $R$(O$_2$N) | 1.173 | 1.200 |
| $R$(O$_3$N) | 1.169 | 1.199 |
| $R$(O$_4$Br) | 2.630 | 2.523 |
| $R$(O$_4$H$_1$) | 0.942 | 0.964 |
| $R$(O$_4$H$_2$) | 0.942 | 0.964 |
| $\alpha$(BrO$_1$N) | 118.4 | 115.8 |
| $\alpha$(O$_1$NO$_2$) | 118.7 | 118.8 |
| $\alpha$(O$_1$NO$_3$) | 112.5 | 110.4 |
| $\alpha$(O$_1$BrO$_4$) | 177.1 | 177.7 |
| $\alpha$(H$_1$O$_4$Br) | 120.6 | 107.6 |
| $\alpha$(H$_2$O$_4$Br) | 120.6 | 107.6 |
| $\alpha$(H$_1$O$_4$H$_2$) | 106.8 | 105.3 |
| $\delta$(O$_2$NO$_1$Br) | 0.0 | 0.0 |
| $\delta$(O$_3$NO$_1$Br) | 180.0 | 180.0 |
| $\delta$(NO$_1$BrO$_4$) | 180.0 | 180.0 |
| $\delta$(H$_1$O$_4$BrO$_1$) | 111.2 | 123.9 |
| $\delta$(H$_2$O$_4$BrO$_1$) | −111.2 | −123.1 |

**TABLE 8: Calculated Vibrational Frequencies ($cm^{-1}$) of $BrONO_2$−$H_2O$ Complex**

| mode | approx assignment | HF/6-311G(d,p) | B3LYP/6-311G(d,p) |
|---|---|---|---|
| 1 | OH$_w$ sym str | 4132 | 3791 |
| 2 | NO$_2$ asym str | 1897 | 1742 |
| 3 | HOH$_w$ bend | 1753 | 1622 |
| 4 | NO$_2$ sym str | 1555 | 1332 |
| 5 | NO$_2$ scissors | 1097 | 850 |
| 6 | BrO str | 908 | 752 |
| 7 | ONO$_2$ ip bend | 807 | 618 |
| 8 | ON str | 445 | 409 |
| 9 | BrO$_w$ str | 266 | 380 |
| 10 | BrON bend | 223 | 224 |
| 11 | BrOH$_w$ rock | 153 | 186 |
| 12 | dimer rock | 74 | 72 |
| 13 | OH$_w$ asym str | 4231 | 3892 |
| 14 | ONO$_2$ op bend | 903 | 754 |
| 15 | BrO$_w$ wag | 380 | 464 |
| 16 | NOBr tosion | 144 | 164 |
| 17 | dimer torsion | 63 | 64 |
| 18 | BrOH$_w$ wag | 22 | 36 |

of vibrational modes of HOBr−$H_2O$ complex and corresponding monomers. In general, the B3LYP frequencies agree with the experiment better than the MP2 frequencies for both HOBr and $H_2O$. The most significant discrepancy appears in the OH stretch mode of HOBr, the calculated frequency overestimates by 5%. But with the same method, the predicted OH stretch frequency of $H_2O$ is in good agreement with the experiment. For the ease of comparison, the vibrational frequency shifts of HOBr and $H_2O$ upon complexation, which were computed at MP2/6-311++G(d,p) level, are shown in Table 3. The basic trend of shifts is the same as that of HOCl−$H_2O$ complex,[21] indicating the similar character of both complexes. As a result of geometry change in HOBr after complexation, especially in O−H bond length, significant changes take place in the OH stretch mode and the bend mode of HOBr. An experimental study of HOBr−$H_2O$ complex is required to testify above theoretical predictions.

Table 4 shows the binding energies of the two HOBr−$H_2O$ conformers at different theory levels. The binding energies are ZPE corrected at the B3LYP/6-311++G(d,p) level. Adding diffuse functions to both heavy atoms and hydrogen reduces the binding energies substantially. The binding energies seem to converge at the MP4/6-311++G(2d,2p) level, since increasing the basis set to 6-311++G(2df,2pd) changes little on the binding energies. The less expensive B3LYP/6-311++G(d,p) single-point calculation well reproduces the results of MP4 calculation using larger basis set which require more CPU and disk storage, indicating the potential application of the former towards larger system. The syn conformer is about 0.2 kcal $mol^{-1}$ more stable, in agreement with that of the HOCl−$H_2O$ complex[21] and in contrast to the water dimer.[31] On the basis of our results, the intermolecular hydrogen bond in HOBr−$H_2O$ complex is a bit weaker than that in HOCl−$H_2O$ complex.

**$BrONO_2$−$H_2O$ Complex.** The equilibrium structure of $BrONO_2$ was investigated at the HF, MP2, and B3LYP levels with 6-311G and 6-311G(d) basis sets, as shown in Table 5. A planar structure of $BrONO_2$ is confirmed. Considering the uncertainties of experimental values of vibrationally averaged structure, both the MP2/6-311G(d) and B3LYP/6-311G(d) optimized geometries are in accord with experiment. Including electron correlation and adding diffuse functions to the basis set are essential to quantitatively predict the $BrONO_2$ structure, and the accuracy here is lower than the HOBr−$H_2O$ system. The largest discrepancy with the experiment appears in Br−$O_1$ and $O_1$−N bond lengths. The B3LYP method overestimates these two bond lengths by about 0.03 Å, while the MP2 method overestimates the $O_1$−N bond length by 0.06 Å. Table 6 lists the harmonic frequencies and IR intensities of $BrONO_2$. The B3LYP/6-311G(d) method again predicts both the vibrational frequencies and their intensities quite well. Our calculations have shown that for the $BrONO_2$ system which has a third-row atom, the B3LYP method is a prior choice if electron correlation should be considered.

Manna[32] recently investigated the interaction of chlorine nitrate ($ClONO_2$) with water at the HF/4-31G level with an optimization of only the parameter directly involved in the interaction and found that the strongest interaction between $ClONO_2$ and water involves the oxygen atom of water and chlorine atom of $ClONO_2$, which is a factor of about 3 stronger than the interaction involving the oxygen atom of $ClONO_2$ with a hydrogen atom of water. We performed full optimization of the $ClONO_2$−$H_2O$ complex at HF with 6-31G(d) basis set and found three equilibrium geometries.[22] Further MP2 and B3LYP level optimizations were performed with 6-31G(d) and 6-311G(d,p) basis sets on the most stable geometry.[22] A $C_s$ symmetry for the complex was found with the HF and MP2 methods. With

**TABLE 9: Calculated Absolute Energies and Binding Energies of $BrONO_2$−$H_2O$ Complex (Absolute Energies in hartrees, Binding Energies in kcal/mol)**

| theory level | $H_2O$ | $BrONO_2$ | $BrONO_2$-$H_2O$ | binding energy[a] |
|---|---|---|---|---|
| HF/6-311G(d,p) | −76.047 01 | −2 851.235 81 | −2 927.295 65 | 6.2 |
| B3LYP/6-311++G(d,p)//HF/6-311G(d,p) | −76.457 65 | −2 854.453 61 | −2 930.923 04 | 5.6 |
| B3LYP/6-311++G(2d,p)//HF/6-311G(d,p) | −76.458 62 | −2 854.460 33 | −2 930.929 52 | 4.8 |
| B3LYP/6-311++G(2df,2p)//HF/6-311G(d,p) | −76.461 85 | −2 854.474 21 | −2 930.945 54 | 4.2 |
| B3LYP/6-311G(d,p) | −76.447 45 | −2 854.454 09 | −2 930.917 64 | 8.2 |
| B3LYP/6-311++G(d,p)//B3LYP/6-311G(d,p) | −76.458 49 | −2 854.463 82 | −2 930.933 52 | 5.2 |
| B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d,p) | −76.459 53 | −2 854.469 69 | −2 930.939 80 | 4.8 |
| B3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) | −76.462 57 | −2 854.482 23 | −2 930.954 19 | 4.0 |

[a] ZPE correction is included.

hybrid density functional method B3LYP, it was found that the $ClONO_2$−$H_2O$ complex slightly breaks the $C_s$ symmetry. With a similar procedure and similar to the results of $ClONO_2$−$H_2O$ complex,[22] among the stable structures the bromine atom of $BrONO_2$ acts as an electron acceptor and the oxygen atom of water acts as an electron donor in the most stable structure. The optimized $BrONO_2$−$H_2O$ geometry, its parameters and its vibrational frequencies are shown in Figure 2 and Tables 7 and 8. As expected, the $C_s$ symmetry structure is a true minimum at the Hartree−Fock level but is a transition state with the B3LYP method since it has one imaginary frequency. The equilibrium structure of the $BrONO_2$−$H_2O$ complex at B3LYP level slightly deviates from the $C_s$ symmetry.

Like the conventional hydrogen bond, the O−Br···O configuration is nearly linear in the complex, as illustrated in Figure 2. The most significant change of $BrONO_2$ upon complexation is that the Br−$O_1$ bond length increases while the $O_1$−N bond length decreases. The binding energies were calculated up to the B3LYP/6-311++G(2df,2p) level with HF/6-311G(d,p) and B3LYP/6-311G(d,p) optimized structures, respectively, as shown in Table 9. Similarly, the binding energies reduces substantially by adding the diffuse functions to both heavy atoms and hydrogen. The binding energy is larger by 1.8 kcal $mol^{-1}$ than that of the $ClONO_2$−$H_2O$ complex.[22] On the basis of our results of $BrONO_2$−$H_2O$ complex, it may indicate that as soon as the $BrONO_2$ molecule is absorbed by the cold aerosols in the stratosphere, it sticks to the ice surface through Br atom.

## Conclusion

We have found two $C_s$ conformers of the HOBr−$H_2O$ complex in which the syn conformer is more stable. The $BrONO_2$−$H_2O$ complex also has a $C_s$ equilibrium structure at the HF level but slightly breaks the $C_s$ symmetry when hybrid DFT method B3LYP is used. The binding energies of the two complexes HOBr−$H_2O$ and $BrONO_2$−$H_2O$ are substantial, suggesting the importance of the interactions of these reservoir molecules with water in the stratosphere.

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## References and Notes

(1) Yung, Y. L.; Pinto, J. P.; Watson, R. T.; Sander, S. P. *J. Atom. Sci.* **1980**, *37*, 339.

(2) Poulet, G.; Pirre, M.; Maguin, F.; Ramaroson, R.; Le Bras, G. *Geophys. Res. Lett.* **1992**, *19*, 2305.

(3) Garcia, R. R.; Solomon, S. *J. Geophys. Res.* **1994**, *99*, 12937.

(4) Yagi, K.; Williams, J.; Wang, N.-Y.; Cicerone, R. J. *Science* **1995**, *267*, 1979.

(5) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*; Evaluation Number 11, Dec 15, 1994: NASA JPL Publication 94-26.

(6) Bridier, I.; Veyret, B.; Lesclaux, R. *Chem. Phys. Lett.* **1993**, *201*, 563.

(7) Molina, M. J.; Tso, T.-L.; Molina, L. T.; Wang, F. C.-Y. *Science* **1987**, *238*, 1253.

(8) Tolbert, M. A.; Rossi, M. J.; Malhotra, R.; Golden, D. M. *Science* **1987**, *238*, 1258.

(9) Leu, M.-T. *Geophys. Res. Lett.* **1988**, *15*, 17.

(10) Koga, Y.; Takeo, H.; Kondo, S.; Sugie, M.; Matsumura, C.; McRae, G. A.; Cohen, E. A. *J. Mol. Spectrosc.* **1989**, *138*, 467.

(11) Jacox, M. E. *J. Phys. Chem. Ref. Data* **1994**, Monograph No. 3.

(12) McGrath, M. P.; Rowland, F. S. *J. Phys. Chem.* **1994**, *98*, 4773.

(13) Lock, M.; Barnes, R. J.; Sinha, A. *J. Phys. Chem.* **1996**, *100*, 7972.

(14) Kukui, A.; Kirchner, U.; Benter, T.; Schindler, R. N. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 455.

(15) Orlando, J. J.; Berkholder, J. B. *J. Phys. Chem.* **1995**, *99*, 1143.

(16) Russic, R.; Berkowitz, J. *J. Chem. Phys.* **1994**, *101*, 7795.

(17) Lee T. J. *J. Phys. Chem.* **1995**, *99*, 15074.

(18) Casper, B.; Lambotte, P.; Minkwitz, R.; Oberhammer, H. *J. Phys. Chem.* **1993**, *97*, 9992.

(19) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1987**, *26*, 1573.

(20) Rayez, M. T.; Destriau, M. *Chem. Phys. Lett.* **1993**, *206*, 278.

(21) Dibble, T. S.; Francisco, J. S. *J. Phys. Chem.* **1995**, *99*, 1919.

(22) Ying, L.; Zhao, X. *J. Phys. Chem.*, submitted.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J. *Gaussian 94*, Revision B.3; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(24) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(25) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155. (c) Becke, A. D. *J. Chem. Phys.* **1992**, *97*, 9173.

(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(27) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(28) McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1991**, *94*, 511.

(29) Curtiss, L. A.; McGrath, M. P.; Blaudeau J.-P.; Davis, N.; Binning, R. C., Jr.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104.

(30) Benedict, W. S.; Gailer, N.; Plyer, E. K. *J. Chem. Phys.* **1956**, *24*, 1139.

(31) Xantheas, S. S.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 8774.

(32) Manna, G. L. *J. Mol. Struct. (THEOCHEM)* **1994**, *309*, 31.