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# Predicting New Molecular Species of Potential Interest to Atmospheric Chemistry: The Isomers HSBr and HBrS

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Coupled cluster singles and doubles with perturbative contributions of connected triples CCSD(T) theory with a series of correlation consistent basis sets was used to predict the existence and characterize for the first time the structures, harmonic frequencies, and energetic quantities of the isomeric species HSBr and HBrS, as well as the transition state connecting them. These calculations consider extrapolation to the complete basis set (CBS) limit, corrections for scalar relativistic effects using the second-order Douglas−Kroll−Hess Hamiltonian, and also correlation of the bromine d electrons in addition to the 14 valence electrons. The species HSBr was found to be more stable than HBrS by 50.93 kcal/mol, with a high barrier height of 60.00 kcal/mol for the interconversion into HBrS. The smaller barrier of 7.90 kcal/mol (ZPE included) for the reverse process, however, should favor a rapid interconversion of HBrS into HSBr if HBrS can also be initially present in a potential synthetic route. If trapped in a matrix, their harmonic frequencies will allow for an unambiguous distinction between the two species. Scalar relativistic corrections and correlation of 24 electrons, although minor for the present purpose of a first time, but accurate, characterization of these species, are needed if chemical accuracy is also pursued. A test of the DFT/B3LYP approach in describing this type of system resulted in good energetic quantities, but geometric parameters and frequencies still lack spectroscopic accuracy. Whether HSBr can act as a temporary bromine reservoir and/or a source of reactive bromine and HS radicals requires further studies that are underway in our group.

## 1. Introduction

Hypochlorous and hypobromous acids (HOCl and HOBr) are known to have important roles in the chemistry of various regions of the Earth's atmosphere.[1] Especially, in the lower stratosphere, the hypohalous acids can be photolyzed, leading to the formation of the radicals OH and X (X=Cl, Br), which are known to be very reactive species participating in the catalytic cycle for the destruction of ozone.[2−9] Initially motivated by an analogy with HOCl, in recent works, we have characterized at a high level of electronic theoretical treatment the isovalent species HSCl and its isomer HClS and examined the possible participation of HSCl as a species coupling the chemistry of sulfur and chlorine in the atmosphere.[10−13] Of the two sulfur-containing isomers, only HSCl has been investigated experimentally as one of the species formed in a $Cl/Cl_2/H_2S$ reaction system in a discharge-flow reactor with a photoionization mass spectrometer; photoionization efficiency spectra and ionization energies were measured in this experiment.[14] Very recently, we have proposed the existence of the radical SBr,[15] characterizing in a detailed way its structure and electronic and vibrational spectra at a high level of electron correlation treatments, also in analogy with our previous investigation of the SCl molecule.[16]

In this work, we have by analogy extended this approach to theoretically predict the existence of the species HSBr and HBrS, isovalent to the pair of molecules HOBr and HBrO. Of this pair, HOBr, in particular, has received considerable attention both theoretically[17−21] and experimentally[22−27] concerning its role in the chemistry of the stratosphere. Our main focus this time is on the characterization of the structures, vibrational spectra, and relative stabilities, as well as the transition state connecting the two isomers, HSBr and HBrS. This investigation was carried out at a high level of theory treatment using the coupled cluster method with all single and double excitations and a perturbative treatment of triple excitations, CCSD(T), and correlation consistent basis sets, with further corrections for the complete basis set limit and scalar relativistic effects. Additionally, density functional theory was also employed to assess the quality of its results as compared with the CCSD(T) ones, having in mind the extension of this type of study to other sulfur/bromine species containing more than three heavy atoms, where a CCSD(T) approach with extended basis sets can be very expensive and time-consuming. Considering the reliability and accuracy of the results reported here, it is our hope that this study can motivate and guide experimentalists in the search of these as yet unknown species and also further motivate the investigation of their participation in the sulfur−bromine chemistry in the atmosphere since they can also be seen as a reservoir/source of bromine, which in its radical form is known to be much more reactive than the chlorine radical in the removal of stratospheric ozone.[28,29]

## 2. Methodology

The basis sets used in this investigation consisted of a series of correlation consistent families, namely, the already standard cc-pV*n*Z (V*n*Z) and the aug-cc-pV*n*Z (AV*n*Z) sets and the set cc-pV*n*Z_DK (V*n*Z-DK), for *n* = D, T, and Q, a recontraction of the corresponding parent set and especially designed for incorporating scalar relativistic corrections for use with the Douglas−Kroll−Hess method.[30−33] Geometries were obtained

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**TABLE 1: Total Energies (au), Geometric Parameters (Å, deg), Harmonic Frequencies ($cm^{-1}$), and Zero-Point Energies (kcal/mol) for the Species HSBr Obtained at the CCSD(T) Level of Theory**[a]

| basis set | energy | rHS | rSBr | ∠HSBr | $\omega_{e1}$ | $\omega_{e2}$ | $\omega_{e3}$ | ZPE |
|---|---|---|---|---|---|---|---|---|
| VDZ-14 | −2970.773 369 | 1.3554 | 2.2445 | 94.68 | 396.7 | 854.7 | 2707.3 | 5.66 |
| VTZ-14 | −2970.974 706 | 1.3427 | 2.2136 | 94.98 | 418.0 | 857.9 | 2698.6 | 5.68 |
| VQZ-14 | −2971.016 570 | 1.3413 | 2.2005 | 95.13 | 424.9 | 869.7 | 2702.1 | 5.71 |
| CBS-14 | −2971.037 882 | 1.3407 | 2.1927 | 95.22 | 428.8 | 877.6 | 2704.8 | 5.75 |
| VDZ-24 | −2970.785 323 | 1.3553 | 2.2420 | 94.70 | 398.2 | 856.0 | 2707.3 | 5.66 |
| VTZ-24 | −2971.034 826 | 1.3427 | 2.2084 | 95.00 | 420.5 | 858.0 | 2698.8 | 5.69 |
| VQZ-24 | −2971.129 958 | 1.3412 | 2.1926 | 95.15 | 429.3 | 873.0 | 2702.2 | 5.73 |
| CBS-24 | −2971.185 640 | 1.3406 | 2.1831 | 95.24 | 434.5 | 883.1 | 2704.8 | 5.75 |
| DKH-VDZ_DK | −3003.698 397 | 1.3555 | 2.2419 | 94.65 | 397.1 | 853.6 | 2703.2 | 5.65 |
| DKH-VTZ_DK | −3003.974 142 | 1.3428 | 2.2075 | 94.94 | 419.2 | 854.6 | 2694.3 | 5.67 |
| DKH-VQZ_DK | −3004.074 804 | 1.3413 | 2.1917 | 95.10 | 428.0 | 868.9 | 2697.4 | 5.71 |
| CBS-DK-24 | −3004.133 313 | 1.3407 | 2.1822 | 95.20 | 433.2 | 878.5 | 2699.8 | 5.73 |

[a] Basis set entries with termination 14 and 24 correspond to calculations with 14 and 24 electrons correlated, the latter one including the 3d electrons of the bromine atom.

**TABLE 2: Total Energies (au), Geometric Parameters (Å, deg), Harmonic Frequencies ($cm^{-1}$), and Zero-Point Energies (kcal/mol) for the Species HBrS Obtained at the CCSD(T) Level of Theory**[a]

| basis set | energy | rHBr | rSBr | ∠HBrS | $\omega_{e1}$ | $\omega_{e2}$ | $\omega_{e3}$ | ZPE |
|---|---|---|---|---|---|---|---|---|
| VDZ-14 | −2970.686 327 | 1.4456 | 2.2976 | 104.4 | 271.2 | 615.0 | 2490.9 | 4.83 |
| VTZ-14 | −2970.891 726 | 1.4428 | 2.2259 | 105.0 | 335.6 | 659.9 | 2446.0 | 4.92 |
| VQZ-14 | −2970.934 392 | 1.4433 | 2.2078 | 104.8 | 349.0 | 661.9 | 2446.1 | 4.94 |
| CBS-14 | −2970.956 105 | 1.4437 | 2.1981 | 104.7 | 355.8 | 660.2 | 2447.7 | 4.95 |
| VDZ-24 | −2970.698 876 | 1.4437 | 2.2951 | 104.4 | 272.6 | 616.7 | 2499.3 | 4.84 |
| VTZ-24 | −2970.953 314 | 1.4348 | 2.2240 | 104.8 | 336.1 | 662.0 | 2483.4 | 4.98 |
| VQZ-24 | −2971.049 166 | 1.4337 | 2.2032 | 104.6 | 351.4 | 671.7 | 2462.6 | 4.98 |
| CBS-24 | −2971.105 163 | 1.4333 | 2.1916 | 104.5 | 359.5 | 676.7 | 2449.1 | 4.98 |
| DKH-VDZ_DK | −3003.611 416 | 1.4425 | 2.2989 | 104.2 | 270.1 | 610.1 | 2486.9 | 4.81 |
| DKH-VTZ_DK | −3003.892 020 | 1.4325 | 2.2280 | 104.6 | 332.1 | 654.8 | 2474.7 | 4.95 |
| DKH-VQZ_DK | −3003.993 351 | 1.4314 | 2.2073 | 104.4 | 347.0 | 663.9 | 2454.0 | 4.95 |
| CBS-DK-24 | −3004.052 143 | 1.4310 | 2.1958 | 104.3 | 354.9 | 668.5 | 2440.5 | 4.95 |

[a] Basis set entries with termination 14 and 24 correspond to calculations with 14 and 24 electrons correlated, the latter one including the 3d electrons of the bromine atom.

by full optimization using the coupled cluster singles and doubles with perturbative contributions of connected triples CCSD(T) with frozen cores of 28 and 38 electrons, the former one including the 3d electrons of bromine.[34,35] We have also estimated the convergence toward the complete basis set (CBS) limit using the three-parameter expression investigated by Peterson et al.,[36] which usually underestimates this limit and is given by

$$E(n) = E_{\mathrm{CBS}} + B\exp\{-(n-1)\} + C\exp\{-(n-1)^2\}1 \qquad (n = 2, 3, \text{and } 4)$$

Changes in geometries and energies due to scalar relativistic effects were also investigated at the CCSD(T) level using the second-order Douglas−Kroll−Hess (DHK) Hamiltonian.[37,38] The nature of all stationary points was examined through the calculation of vibrational frequencies in the harmonic oscillator approximation. All the CCSD(T) calculations were carried out with the Molpro suite of programs.[39]

As a reference for further investigations in our group of species containing more than two bromine and/or sulfur atoms, which can become quite prohibitive at the CCSD(T) level with extended basis sets, additional calculations were also performed with density functional theory, using the B3LYP functionals,[40,41] and the family cc-pV*n*Z ($n$ = D, T, and Q)[31,32] of correlation consistent basis sets to assess the performance of DFT/B3LYP as compared to CCSD(T) as a cheaper and reliable first source of structural and energetic data for this type of species. The calculation of this step was performed with the Gaussian 98 suite of programs.[42]

## 3. Results and Discussion

Total energies, optimized structures, harmonic vibrational frequencies, and zero-point energies (ZPE) for three stationary points obtained at the CCSD(T) level are collected in Tables 1−3 for the various families of basis sets described in Section 2. Clearly, the global minimum corresponds to HSBr (thiohypobromous acid), and the local one is associated with the species HBrS; the third stationary point corresponds to the transition state structure connecting these two minima; these results are discussed next.

**(A) CCSD(T) with 14 Electrons Correlated.** At the complete basis set (CBS) limit, our cc-pV*n*Z CCSD(T) ($n$ = D, T, and Q) calculations with 14 electrons correlated predict the species HSBr to be more stable than HBrS by 51.32 kcal/mol. Structurally, they show a quite distinct feature, a bond angle of 95.2° in HSBr contrasted with 104.7° in HBrS; also, the S−Br bond distance is estimated to be slightly longer (2.198 Å) in the datively bonded Br → S atoms as compared with 2.193 Å in the usual Br−S covalent bond in HSBr. These values are intermediate with the value of 2.148 Å found theoretically for the free SBr radical[15] and 2.24 Å found experimentally for $S_2Br_2$. The H−S bond distance of 1.341 Å in HSBr is slightly shorter than the corresponding value (1.346 Å) in the free HS molecule; however, in the case of the H−Br bond distance in HBrS, its larger value of 1.444 Å, as compared with 1.414 Å in the free HBr molecule, reflects a bond distance lengthening in the triatomics, certainly a result of a charge migration from the H−Br moiety to the bond region of the Br−S pair in the triatomics. CBS harmonic frequencies are also predicted to be quite distinct in the two species. The harmonic frequency $\omega_{e3}$ of 2704.8 $cm^{-1}$ in HSBr can be associated with the H−S

**TABLE 3: Total Energies (au), Geometric Parameters (Å, deg), Harmonic Frequencies ($cm^{-1}$), and Zero-Point Energies (kcal/mol) for the Transition State (HSBr ↔ HBrS) Obtained at the CCSD(T) Level of Theory[a]**

| basis set | energy | rHS | rSBr | ∠HSBr | $\omega_{e1}$ | $\omega_{e2}$ | $\omega_{e3}$ | ZPE |
|---|---|---|---|---|---|---|---|---|
| VDZ-14 | −2970.675 584 | 2.2040 | 2.4718 | 35.62 | 233.2 | 741.0*i* | 2457.1 | 3.86 |
| VTZ-14 | −2970.878 357 | 2.1380 | 2.3777 | 37.12 | 293.7 | 822.5*i* | 2394.5 | 3.84 |
| VQZ-14 | −2970.919 862 | 2.1152 | 2.3556 | 37.61 | 304.7 | 864.4*i* | 2369.1 | 3.82 |
| CBS-14 | −2970.940 881 | 2.1021 | 2.3439 | 37.89 | 310.0 | 889.9*i* | 2354.1 | 3.81 |
| VDZ-24 | −2970.688 044 | 2.1996 | 2.4686 | 35.63 | 234.6 | 742.3*i* | 2462.8 | 3.86 |
| VTZ-24 | −2970.939 903 | 2.1244 | 2.3734 | 37.06 | 295.8 | 824.1*i* | 2411.2 | 3.87 |
| VQZ-24 | −2971.034 592 | 2.1006 | 2.3477 | 37.57 | 308.0 | 867.8*i* | 2365.8 | 3.82 |
| CBS-24 | −2971.089 892 | 2.0871 | 2.3336 | 37.87 | 314.1 | 894.5*i* | 2336.9 | 3.79 |
| DKH-VDZ_DK | −3003.601 076 | 2.2070 | 2.4685 | 35.55 | 234.8 | 736.1*i* | 2459.7 | 3.85 |
| DKH-VTZ_DK | −3003.879 316 | 2.1309 | 2.3740 | 36.93 | 295.2 | 813.6*i* | 2412.8 | 3.87 |
| DKH-VQZ_DK | −3003.979 556 | 2.1067 | 2.3486 | 37.43 | 307.0 | 858.1*i* | 2366.9 | 3.82 |
| CBS-DK-24 | −3004.037 692 | 2.0930 | 2.3447 | 37.72 | 312.9 | 885.5*i* | 2337.6 | 3.78 |

[a] Basis set entries with termination 14 and 24 correspond to calculations with 14 and 24 electrons correlated, the latter one including the 3d electrons of the bromine atom.

stretching, which in the free HS molecule is equal to 2711.6 $cm^{-1}$, whereas in HBrS, $\omega_{e3}$ (2447.7 $cm^{-1}$) accounts basically for the H−Br stretching (2649.7 $cm^{-1}$ in the free molecule). Notice that the lower value of $\omega_{e3}$ in HBrS, as compared with HBr, is consistent with a charge migration to the Br−S moiety, thus weakening the H−Br bond. The lowest frequency ($\omega_{e1}$) values, 428.8 $cm^{-1}$ in HSBr and 355.8 $cm^{-1}$ in HBrS, can be associated with the S−Br stretching, which in the free SBr species is predicted to be 462 $cm^{-1}$.[15] Thus, in the normal covalently bonded HSBr species, $\omega_{e1}$ is close to the harmonic frequency of the singly bonded diatomics, whereas in HBrS, the smaller value reflects a weaker bond. As to the bending mode frequencies ($\omega_{e2}$), the value of 877.6 $cm^{-1}$ in HSBr is consistent with the smaller bond angle (95.2°) in HSBr, with the bivalent sulfur atom using its 3p orbitals to singly bind to the H and Br atoms; just for comparison, in $H_2S$, one finds a bond angle of 92.2°. In HBrS, we find an angle of 104.7° associated with a bending frequency of 660.2 $cm^{-1}$.

**(B) CCSD(T) with 24 Electrons Correlated.** Next, we investigated how significantly the structural parameters and the relative stability of these isomers are affected by correlating in our calculation a total of 24 electrons, which includes the 14 valence electrons and the 10 electrons of the Br d subshell. The CBS-24 data in Tables 1 and 2 show a slight stabilization (0.83 kcal/mol) of HBrS leading to a reaction energy of 50.50 kcal/mol and a practically unchanged H−S bond distance of 1.341 Å and a bond angle of 95.2° in HSBr; however, a significant decrease (−0.010 Å) is found for the Br−S bond distance (2.183 Å) when 24 electrons are correlated. In HBrS, the H−Br bond distance (1.433 Å) in the 24 electron correlated calculation decreases substantially (−0.010 Å) as compared to the one with 14 electrons correlated (1.444 Å); the bond angle decreases only slightly, +0.2°. Notice that the correlating 24 electrons result in a more pronounced decrease (−0.01 Å) in the Br−S bond distance (2.183 Å) in HSBr as compared with a decrease of −0.006 Å in HBrS (2.192 Å). As to the harmonic frequencies, as expected, the H−S stretching is unaffected by the 24 electron correlation treatment, but both $\omega_{e1}$ and $\omega_{e2}$ increase by about 6 $cm^{-1}$ in HSBr; in HBrS, the mode associated with the H−Br stretching has a frequency variation of only +1.4 $cm^{-1}$, as compared with the substantial change of +16.5 $cm^{-1}$ in the frequency of the bending mode, which implies the need to have the 3d electrons correlated if chemical accuracy is to be achieved. Finally, the frequency of the Br−S stretch changes by +3.7 $cm^{-1}$. As a cautionary comment, we note that although in the present case the trends observed with our sequence of basis sets look fine, an important point concerning the use of the cc-pV*n*Z basis sets is that they were designed for valence correlation, and its use for 3d correlation of Br can lead to unreliable results or at least very slow basis set convergence.

**(C) Scalar Relativistic Effects.** Although the results described previously are sufficiently accurate and reliable to characterize these two species, considering the presence of the heavy atom Br, one might also ask for possible changes resulting from the inclusion of scalar relativistic effects in the calculation. For such, the stationary points were also explored at the CCSD(T) level with the Douglas−Kroll−Hess (DHK) Hamiltonian and the cc-pV*n*Z_DK basis sets with 24 electrons correlated. At the CBS limit, our calculations show a relative energy increase of 0.43 kcal/mol, with the reaction energy now equaling 50.93 kcal/mol, a small difference for a first time characterization of these species, but which can become a significant one if one goes one step further and calculates heats of formation within chemical accuracy. For the HSBr species, scalar relativistic corrections changed rHS by +0.1 mÅ, rSBr by −0.9 mÅ, and the bond angle by −0.04°; changes in the harmonic frequencies amounted to −1.3, −4.6, and −5.0 $cm^{-1}$, respectively, for $\omega_{e1}$, $\omega_{e2}$, and $\omega_{e3}$. For the molecule with Br as the central atom, these changes are more significant, −2.3 mÅ for rHBr, +4.2 mÅ for rBrS, and −0.2° for the bond angle; for the harmonic frequencies $\omega_{e1}$, $\omega_{e2}$, and $\omega_{e3}$, we found −4.6, −8.2, and −8.6 $cm^{-1}$, respectively. Clearly, for both species, the frequencies are significantly decreased when corrections for scalar relativistic effects are incorporated in the calculations.

**(D) Transition State.** Concerning the transition state, our 14 electron correlated CBS/cc-pV*n*Z ($n$ = D, T, and Q) estimate of the barrier height for the HSBr ↔ HBrS reaction is 60.87 kcal/mol for the forward direction, a result that becomes slightly smaller (60.08 kcal/mol) if 24 electrons are correlated; with corrections for scalar relativistic effects at the CBS limit, a further reduction by only 0.08 kcal/mol is observed. On the other hand, for the reverse reaction, HBrS → HSBr, a significantly lower barrier height is predicted, practically identical for the calculations with 14 electrons (9.55 kcal/mol) and 24 electrons (9.58 kcal/mol) correlated; scalar relativistic corrections, however, decreases this value to 9.07 kcal/mol, a significant variation if chemical accuracy is desired. Inclusion of zero-point energies further decreases this value to 7.90 kcal/mol. An experimental implication of this result is that if a potential route of synthesis can in principle lead to both species, the isolation of the thermodynamically less stable species might become very difficult due to a rapid interconversion of HBrS into the thermodynamically more stable molecule. Interesting also to note in the energetic results in these tables is that increasing the size of the basis sets favors the stabilization of HBrS relative to HSBr, with the reaction energy decreasing from 54.25 kcal/

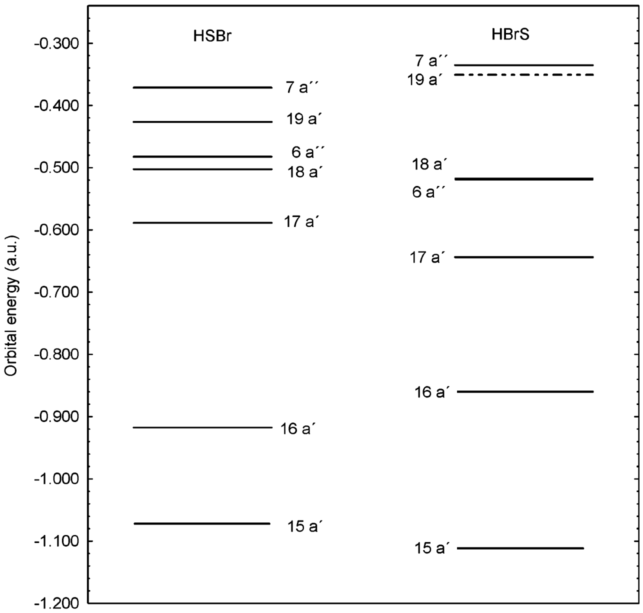

**Figure 1.** Valence orbital energy diagram for HSBr and HBrS.

mol at the cc-pVDZ CCSD(T) level to 50.50 kcal/mol at the CBS limit (24 electrons correlated), whereas the forward barrier decreases much less, from 61.04 to 60.08 kcal/mol. Consequently, the reverse barrier increases from 6.80 to 9.58 kcal/mol. Structurally, the transition state has a cyclic structure with the bond distances very close to those of the higher lying isomer, HBrS, and an ∠HBrS angle of 61.8° and an ∠HSBr angle of 37.9°; the imaginary frequency corresponds to the bending mode.

**(E) Electronic Structure and Dipole Moment.** Complementing the previous characterization, it is also interesting to identify the main distinctive features of the electronic structures of these species. In terms of a self consistent field molecular orbital (MO) picture, the valence electronic configuration of HSBr and HBrS could be symbolized as ...$(15a')^2$ $(16a')^2$ $(17a')^2$ $(18a')^2$ $(6a'')^2$ $(19a')^2$ $(7a'')$,$^2$ and ...$(15a')^2$ $(16a')^2$ $(17a')^2$ $(6a'')^2$ $(18a')^2$ $(19a')^2$ $(7a'')$,$^2$ respectively; the corresponding orbital energies are depicted in the diagram of Figure 1. For both molecules, the lowest-lying valence MO (15a′) can be viewed as a bonding orbital associated with the H−S moiety in HSBr and with the H−Br moiety, in the case of HBrS; molecular orbital 16a′ corresponds to a bonding orbital associated with the S−Br moiety, and in the case of HBrS, the classical view of a dative bond is quite distinctive in a 3-D representation (not shown here). The remaining MOs are essentially nonbonding ones. For both species, MO 17a′ corresponds to a kind of $sp^2$ hybrid associated with the central atom; MO 6a″ is mainly the $4p_z$ atomic orbital of the bromine atom, and MO 7a″ the $3p_z$ atomic orbital of the sulfur atom. Finally, the two highest-lying MOs can be viewed as a kind of p-type lone pair on the terminal heavy atoms.

A numerical estimate of the degree of polarization of the S−Br moiety derived from a Mulliken population analysis with the MP2 density and the cc-pVQZ basis set shows the molecule HBrS to be much more polarized as the figures in parentheses, representing the net Mulliken charges, show H(+0.070)S(−0.007)Br(−0.063) and H(+0.162)Br(+0.261)S(−0.423). Charge migration from Br to S is very significant in HBrS as reflected also in the dipole moments at the SCF−-HF/cc-pVQZ level, 1.21 and 4.09 D, respectively, for HSBr and HBrS; at the MP2/cc-pVQZ level, we obtained 1.17 and 4.12 D, respectively.

**(F) DFT/B3LYP versus CCSD(T).** One final point also investigated in this study is concerned with the performance of DFT/B3LYP in predicting energetic data and structural parameters, as compared with CCSD(T), that can be taken as a reasonable first exploration result especially in the case that this type of system can grow in complexity. In Table 4, we have collected results with the cc-pV*n*Z ($n$ = D, T, and Q) basis set and the corresponding CBS limits for the triatomics discussed in this section. First, energetically, this approach predicts for the forward reaction energy 51.08 kcal/mol and 60.49 kcal/mol for the barrier height, which are surprisingly very close to our CBS-14 values of 51.32 and 60.87 kcal/mol. In contrast to this agreement, the harmonic frequencies are mostly underestimated for the three stationary points: (−17.0, −17.5, −43.0) for HSBr, (−9.7, +31.1, −137.1) for HBrS, and (−9.0, −61.4*i*, −61.6) for the transition structure, where the figures in parentheses are the differences between the harmonic frequencies calculated at the CBS/cc-pV*n*Z DFT/ B3LYP and the CBS/cc-pV*n*Z CCSD(T) levels. Note that the relative discrepancy can be as large as ∼7% for the bending mode frequency of the transition state

**TABLE 4: Total Energies (au), Geometric Parameters (Å, deg), Harmonic Frequencies ($cm^{-1}$), and Zero-Point Energies (kcal/mol) for the Species HSBr, HBrS, and the Transition State Structure Obtained at the DFT/B3LYP Level of Theory with the cc-pV*n*Z (*n* = D, T, and Q) Basis Set**

HSBr

| basis set | energy | rHS | rSBr | ∠HSBr | $\omega_{e1}$ | $\omega_{e2}$ | $\omega_{e3}$ | ZPE |
|---|---|---|---|---|---|---|---|---|
| VDZ | −2972.958 713 | 1.3608 | 2.2403 | 95.19 | 402.7 | 841.6 | 2654.0 | 5.57 |
| VTZ | −2973.054 410 | 1.3474 | 2.2207 | 95.43 | 410.9 | 855.2 | 2664.6 | 5.62 |
| VQZ | −2973.062 356 | 1.3450 | 2.2163 | 95.63 | 411.6 | 858.4 | 2663.1 | 5.62 |
| CBS | −2973.064 397 | 1.3439 | 2.2140 | 95.76 | 411.8 | 860.1 | 2661.7 | 5.62 |

HBrS

| basis set | energy | rHS | rSBr | ∠HSBr | $\omega_{e1}$ | $\omega_{e2}$ | $\omega_{e3}$ | ZPE |
|---|---|---|---|---|---|---|---|---|
| VDZ | −2972.874 120 | 1.4706 | 2.2464 | 107.32 | 319.9 | 652.9 | 2231.1 | 4.70 |
| VTZ | −2972.972 142 | 1.4582 | 2.2182 | 106.55 | 342.0 | 684.0 | 2293.5 | 4.79 |
| VQZ | −2972.980 654 | 1.4562 | 2.2133 | 106.25 | 344.9 | 689.0 | 2305.0 | 4.78 |
| CBS | −2972.982 998 | 1.4554 | 2.2109 | 106.08 | 346.1 | 691.3 | 2310.6 | 4.78 |

Transition State

| basis set | energy | rHS | rSBr | ∠HSBr | $\omega_{e1}$ | $\omega_{e2}$ | $\omega_{e3}$ | ZPE |
|---|---|---|---|---|---|---|---|---|
| VDZ | −2972.861 837 | 2.2801 | 2.4157 | 35.98 | 276.6 | 758.2*i* | 2379.3 | 3.71 |
| VTZ | −2972.957 994 | 2.1917 | 2.3754 | 36.94 | 298.5 | 800.6*i* | 2325.9 | 3.72 |
| VQZ | −2972.965 959 | 2.1731 | 2.3699 | 37.15 | 300.5 | 818.1*i* | 2304.9 | 3.72 |
| CBS | −2972.967 996 | 2.1636 | 2.3676 | 37.26 | 301.0 | 828.5*i* | 2292.5 | 3.71 |

and ~6% for the HBr stretching mode frequency in HBrS. Interatomic distances are overestimated in HBrS and the transition state, being at most 0.062 Å larger in this latter case, and underestimated by at most 0.021 Å in HSBr. In practical terms, taking into account the time/cost factors, these results seem to be satisfactory as an initial characterization of this type of system, and for larger singlet ones, it is likely also to give reasonable results, at least for the energetic quantities. However, for chemical and spectroscopic accuracies, highly correlated approaches such as CCSD(T) and/or CASSCF/MRCI are required, although quite demanding for larger systems.

**(G) Implications to Atmospheric Chemistry.** Finally, although in this study our major concern was the characterization of these isomers and the associated transition state, it is worth mentioning that further studies are presently being conducted in our group concerning the possible formation of HSBr, its photolytic dissociation, and its role as a temporary bromine reservoir/source in the stratosphere. For its isovalent partner, HSCl, we have shown that it can be formed at high pressures and also under conditions in the stratosphere in which HS can be found in significant concentrations, an event likely to occur after strong volcanic eruptions.[12,13] We have presented arguments that HSCl can act as a temporary chlorine reservoir when stored in Antarctica during the winter if it survives any nonphotochemical process. At springtime, however, it can be photodissociated by sunlight, then producing the very reactive chlorine and HS radicals. If that also applies to HBrS is a subject that merits further investigation, and in this perspective, we hope this study can motivate further research of this system.

## 4. Conclusion

New isomeric species HSBr and HBrS, as well as the transition state connecting them, are predicted for the first time and characterized structurally and energetically at a high level of electronic correlation treatment CCSD(T) with a series of correlation consistent basis sets. Complete basis set limit geometries, energies, and frequencies, with further corrections for scalar relativistic effects, offer a very reliable and accurate description of this system. Energetically, with corrections for scalar relativistic effects and the correlation of 24 electrons, the species HSBr was found to be favored by 50.93 kcal/mol, with the HSBr → HBrS interconversion facing a relatively high energy barrier of 60.00 kcal/mol. Experimentally, if both species can in principle be formed initially, the small barrier of 7.90 kcal/mol (ZPE included) for the reverse reaction will favor the interconversion to the thermodynamically more stable HSBr. However, if they can be isolated in a matrix, their infrared spectra will permit an unambiguous identification of both species. Correlating the 3d electrons of Br resulted in a significant change of $+16.5\ \mathrm{cm}^{-1}$ in the bending mode frequency of HBrS. Overall, scalar relativistic corrections resulted in a decrease of the vibrational frequencies. Energetic results at the CBS/cc-pV*n*Q DFT/B3LYP ($n$ = D, T, and Q) level were very close to our CCSD(T) values, but geometric parameters and frequencies differed significantly. From a chemistry of the atmosphere perspective, in principle, HSBr can be viewed both as a potential temporary reservoir of bromine and as a species coupling the chemistry of bromine and sulfur in the atmosphere and also as a potential source of reactive Br and HS radicals. In view of the high level results presented here, we hope that this study can motivate and guide experimental investigation of this species in the near future.

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