New Molecular Species of Potential Interest to Atmospheric Chemistry: Isomers on the [H, S_2, Br] Potential Energy Surface

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This work reports a state-of-the-art theoretical characterization of four new sulfur−bromine species and five transition states on the [H, S_2, Br] potential energy surface. Our highest level theoretical approach employed the method coupled cluster singles and doubles with perturbative contributions of connected triples, CCSD(T), along with the series of correlation-consistent basis sets and with extrapolation to the complete basis set (CBS) limit in the optimization of the geometrical parameters and to quantify the energetic quantities. The structural and vibrational frequencies here reported are unique and represent the most accurate investigation to date of these species. The global minimum corresponds to a skewed structure HSSBr with a disulfide bond; this is followed by a pyramidal-like structure, SSHBr, 18.85 kcal/mol above the minimum. Much higher in energy, we found another skewed structure, HSBrS (50.29 kcal/mol), with one S−Br dative-type bond, and another pyramidal-like one, HBrSS (109.80 kcal/mol), with two S−Br dative-type bonds. The interconversion of HSSBr into SSHBr can occur via a transfer of either the hydrogen or the bromine atom but involves a very high barrier of about 43 kcal/mol. These molecules are potentially a new route of coupling the sulfur and bromine chemistry in the atmosphere, and conditions of high concentration of H_2S like in volcanic eruptions might contribute to their formation. We note that HSSBr can act as a reservoir molecule for the reaction between the radicals HSS and Br. Also, an assessment of the methods DFT/B3LYP/CBS and MP2/CBS relative to CCSD(T)/CBS provides insights on the expected performance of these methods on the characterization of polysulfides and also of more complex systems containing disulfide bridges.

1. Introduction

The importance of halogen-containing species like ClO, BrO, IO, HOCl, HOBr, and HOI in reactions involved in the catalytic cycle for the destruction of ozone in the stratosphere is quite well documented in the literature.[1−3] An understanding of reactions between radical carriers leading to another carrier or to a reservoir molecule is of great relevance in this context. In the case of the species BrO and OH, it can lead to two other carriers HO_2 and Br, and a further reaction of HO_2 with Br can either generate HBr and O_2 in one case, or HO and BrO in the other. In the analysis of the kinetic results for this reaction, it was suggested the formation of a vibrationally excited addition complex of the type HOOBr to account for the large magnitude of the rate constant observed.[4] This possibility motivated theoretical studies concerned with structural features and relative stabilities of the various isomers on the [H, O_2, X] (X = Cl, Br) potential energy surface and also on possible reactions between different carriers having these isomers as intermediates.[5−8]

Initially motivated by analogies with the above oxygenated molecules, in recent studies we have investigated new species like SCl, SBr, SI, HSCl, HClS, HSBr, HBrS, HSI, and HIS and characterized their thermodynamic properties, vibrational spectra, and structural parameters.[9−14] We have also raised the possibility of their potential role in the coupling of the halogen−sulfur chemistries in the atmosphere. In the case of HSCl, we have shown that after strong volcanic eruptions, a condition in which the concentration of HS becomes significant, it is very likely that the species HSCl can be formed, as well as under high pressures.[15,16]

In this work, as part of an ongoing investigation on sulfur-containing species, and guided also by the same type of analogy we have carried out so far for the sulfur−halogen compounds mentioned above, we focus on the theoretical characterization of the [H, S_2, Br] potential energy surface (PES) at a high level of correlation treatment and using extended correlation-consistent basis sets. Theoretically, an atoms-in-molecules (AIM) analysis of the isomerization reaction SSHBr → HSSBr was carried out by Zeng et al.[17] with geometrical parameters optimized with the DFT/B3LYP/6-311++G(2df, pd) approach, followed by energy calculations at the MP2/6-311++G(2df, pd) level on top of the DFT/B3LYP/6-311++G(2df, pd) optimized geometries for four stationary points (two minima and two transition states). Systems showing a disulfide bond (XSSX, X = F, Cl, Br) have been investigated theoretically by Prascher and Wilson,[18] and more recently, the isomerization reaction $SSX_2 \rightarrow XSSX$ (X = F, Br) was also extensively investigated in our group with a highly correlated treatment, CCSD(T)/CBS.[19,20] We note further that in the case of the isomers FSSF and $S{=}SF_2$, the DFT/B3LYP approach has failed to correctly predict the order of stability of these two isomers.[19] In this study, considering the high-level approach used and the reliability and accuracy of the results here reported, it is our hope that it can motivate and guide experimentalists in the search of these as yet unknown species and also examine their potential role in the halogen−sulfur chemistry in the atmosphere.

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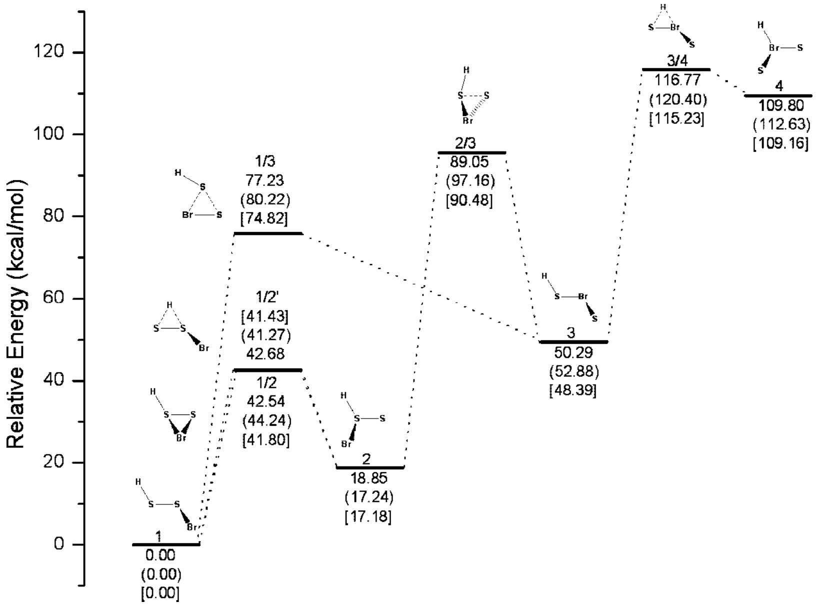

Figure 1. Relative energy profile at the CCSD(T)/CBS level of theory. Values in parentheses are at the MP2/CBS level, and values in square brackets are at the DFT/B3LYP/CBS level of theory.

2. Methods

As to the methodologies used to account for electron correlation, we have employed three theoretical approaches: density functional theory (DFT), with the B3LYP hybrid functional,[21,22] second-order Møller−Plesset perturbation theory,[23] and a high-level one, the method coupled cluster singles and doubles with perturbative contributions of connected triples, CCSD(T).[24−27] A comparison of the results obtained with these approaches is expected to give us an indication of the performance of DFT/B3LYP and MP2 relative to CCSD(T) in the investigation of polysulfide systems where the use of CCSD(T) with large basis sets can become prohibitive. For basis functions, the series of augmented correlation-consistent polarized valence basis sets aug-cc-pV*n*Z for the bromine and hydrogen atoms were used, and the aug-cc-pV(n+d)Z for the sulfur atom, with n = D, T, and Q;[28,29] the latter one includes a tight *d*-type function, which has been shown to be very important for improving convergence and accuracy for sulfur-containing species. In the presentation of the results and the discussion that follows, we will refer to these sets collectively as aV*n*Z. The energetic results were next extrapolated to the complete basis set (CBS) limit using the three-parameter formula shown below:[30]

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

All calculations were carried out with the MOLPRO suite of programs.[31]

3. Results and Discussion

In this study, we have investigated nine stationary points, four of them associated with minima and five with transition states connecting these minima. In Figure 1, an overall energetic profile of these states is shown, and the optimized geometries obtained are displayed in Figure 2. The best extrapolated results calculated for energy-related quantities are collected in Table 1, and in Table 2 are the harmonic vibrational frequencies. Detailed data calculated with all the basis sets are available upon request to the authors. We note that the nature of the stationary points has been properly checked to identify them either as true minimum or as a first-order saddle point, and that intrinsic reaction coordinate (IRC) calculations were also carried out with the MP2/aVDZ approach to identify the transition states as the ones really connecting reactants and products.

3.A. Energetics. The energetic data in Table 1 unequivocally places the skewed structure HSSBr (**1**) as the global minimum; next in stability, our calculations located a distorted pyramidal-like structure SSHBr (**2**) lying 18.85 kcal/mol (17.24 and 17.18 kcal/mol) higher in energy, respectively, at the CCSD(T)/CBS (MP2/CBS and DFT/B3LYP/CBS) levels of calculation; still higher in energy, we found another skewed structure, the isovalent analogue of the bromous acid (HOBrO), HSBrS (**3**), now with the sulfur as the terminal atom, at 50.29 kcal/mol (52.88 and 48.39 kcal/mol) as predicted by the methods CCSD(T)/CBS (MP2/CBS and DFT/B3LYP/CBS), respectively. Finally, another species, $HBrS_2$ (**4**), was found to be the least stable of the four isomers, being at 109.80 kcal/mol (112.63 and 109.16 kcal/mol) at the CCSD(T)/CBS (MP2/CBS and DFT/B3LYP/CBS) levels of calculation, respectively, above the global minimum. Concerning these minima, it is interesting to point out that, for the oxygenated analogues, a structure like SSHBr was not found on the PES, and that the one similar to HSBrS was located very low in energy (3.8 kcal/mol) relative to the global minimum. In our study, with respect to the most stable isomer, the species $HBrS_2$ was found to lie much higher (109.80 kcal/mol) than the corresponding oxygenated ($HBrO_2$) one, 52.7 kcal/mol. Despite these differences, one can note that the relative energy between structures **3** and **4** in this work, 59.51 kcal/mol, is not so much larger than the corresponding one (48.9 kcal/mol) for the oxygenated compounds. Another point that should be mentioned about the energy difference between structures **1** and **2** is that it follows the same energetic trend as that calculated for the species BrSSBr and $SSBr_2$, with the skewed structure lower in energy by 13.97 kcal/mol.[20] In the case of the sulfur compounds, it seems that the extra stability of structures **1** and **2** can be accounted for by their disulfide bridge, which is known to be more stable than the peroxide one.[32] In particular, structure **2** can also be rationalized in terms of the extended valence of the sulfur atom.

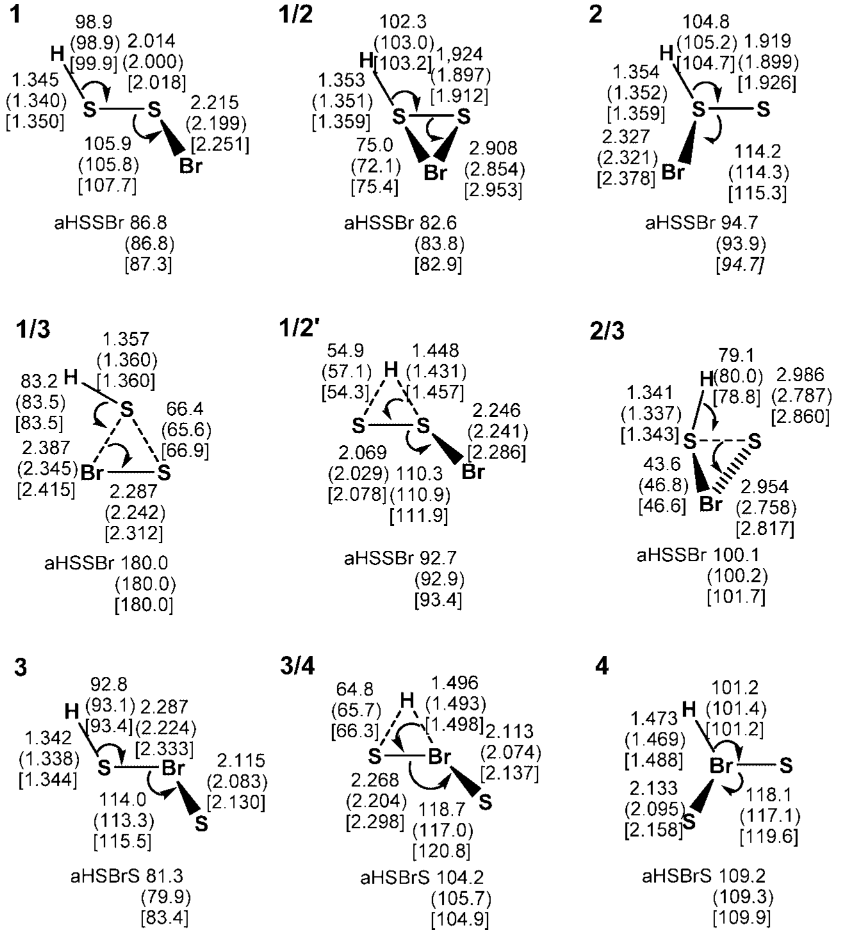

Figure 2. Optimized geometries in angstroms and degrees at the CCSD(T)/CBS level of theory; values in parentheses are the MP2/CBS results, and values in square brackets are the DFT/B3LYP/CBS ones.

TABLE 1: Total Energies (in hartree), Relative Energies Including the Zero-Point Energies (in kcal/mol), and Zero-Point Energies (in kcal/mol) Calculated at the DFT/B3LYP/CBS, MP2/CBS, and CCSD(T)/CBS Levels of Theory

	energy + 3368			relative energy			zero-point energy		
	B3LYP	MP2	CCSD(T)	B3LYP	MP2	CCSD(T)	B3LYP	MP2	CCSD(T)
1	−3.299241	−0.751162	−0.818250	0.00	0.00	0.00	7.07	7.36	7.21
2	−3.271858	−0.724049	−0.788542	17.18	17.24	18.85	7.24	7.59	7.42
3	−3.222130	−0.665585	−0.736631	48.39	52.88	50.29	6.21	6.55	6.29
4	−3.125283	−0.570700	−0.641556	109.16	112.63	109.80	5.87	6.75	6.14
1/2	−3.232622	−0.680133	−0.749071	41.80	44.24	42.54	6.64	7.04	6.32
1/2′	−3.220996	−0.682449	−0.746697	41.43	41.27	42.68	4.81	5.41	4.99
1/3	−3.180011	−0.622228	−0.693902	74.82	80.22	77.23	6.34	6.65	6.41
2/3	−3.143144	−0.594706	−0.675136	90.48	97.16	89.05	5.85	6.35	6.46
3/4	−3.115606	−0.555681	−0.628511	115.23	120.40	116.77	4.75	5.21	4.92

Concerning the isomerization reaction **1** → **2**, it can occur by two reaction paths: one via a transfer of a bromine atom (**1/2**) and the other via a transfer of a hydrogen atom (**1/2′**). It is interesting to note that these two paths lead to structures that are mirror images of each other. The path passing by the transition state **1/2** involves an energy barrier of 42.54 kcal/mol (44.24 kcal/mol at MP2/CBS and 41.80 kcal/mol at DFT/B3LYP/CBS). For the CCSD(T)/CBS calculation, this value is practically identical to the one passing by the transition state **1/2′**, 42.68 kcal/mol. One should note, however, that the relative height of these two energy barriers is reversed as predicted by the MP2/CBS calculation (41.27 kcal/mol), and 41.43 kcal/mol by the DFT/B3LYP/CBS approach. In effect, the isomerization via an H atom transfer is predicted to be more likely by the two lower level approaches.

As to the formation of isomer **3** from **1** via the transition state **1/3**, it represents an isomerization process very unlikely to occur due to the very large energy barrier, 77.23 kcal/mol. Similarly, the isomerization **2** → **3**, via **2/3**, involves surpassing an energy barrier of 70.20 kcal/mol and is also very unlikely to proceed. With the MP2/CBS approach, this barrier is predicted to be about 14% larger, 79.92 kcal/mol, whereas with the DFT/B3LYP/CBS method, we found 73.30 kcal/mol. For the process **3** → **4**, involving the migration of a hydrogen atom, the CCSD(T)/CBS energy barrier is 66.48 kcal/mol, not so much different than 67.52 kcal/mol (MP2/CBS) and 66.84 kcal/mol (DFT/B3LYP/CBS). However, for the reverse process, the CCSD(T)/CBS result amounts to only 6.97 kcal/mol. If $HBrS_2$ can be formed by some reactive channel, it is very likely that it will readily isomerize to the most stable species (**1**), since its energy content is large enough to surpass the reverse reaction barriers.

3.B. Structures. In the absence of any experimental data, to the best of our knowledge, with which the results of this

TABLE 2: Vibrational Harmonic Frequencies (in cm^{-1}) Calculated at the DFT/B3LYP/CBS, MP2/CBS, and CCSD(T)/CBS Levels[a]

		frequencies					
system	method	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
1	B3LYP	163	363	408	512	904	2594
	MP2	173	399	410	547	917	2707
		(1.9)	(7.7)	(27.8)	(17.5)	(5.5)	(0.4)
	CCSD(T)	169	388	396	532	909	2653
2	B3LYP	144	290	636	714	925	2500
	MP2	151	308	714	758	944	2587
			(84.5)	(114.4)	(3.5)	(4.7)	(9.4)
	CCSD(T)	148	306	656	746	928	2555
3	B3LYP	134	228	277	430	740	2667
	MP2	143	240	316	483	801	2739
			(17.6)	(85.2)	(48.2)	(4.4)	(5.6)
	CCSD(T)	129	220	277	477	759	2695
4	B3LYP	143	361	383	599	711	2050
	MP2	163	432	458	660	770	2244
		(1.7)	(6.9)	(105.9)	(8.4)	(17.6)	(20.7)
	CCSD(T)	145	383	410	611	715	2175
1/2	B3LYP	354*i*	155	375	650	640	2525
	MP2	504*i*	205	426	735	935	2621
	CCSD(T)	332*i*	147	324	609	918	2585
1/2′	B3LYP	1553*i*	148	326	488	518	2029
	MP2	1275*i*	155	349	504	587	2196
	CCSD(T)	1284*i*	151	350	507	542	2093
1/3	B3LYP	325*i*	293	352	410	891	2499
	MP2	538*i*	359	419	479	894	2520
	CCSD(T)	475*i*	315	371	398	867	2533
2/3	B3LYP	460*i*	136	211	380	835	2668
	MP2	677*i*	164	232	432	871	2748
	CCSD(T)	495*i*	134	435	439	918	2725
3/4	B3LYP	891*i*	127	306	406	534	2064
	MP2	1106*i*	150	391	485	611	2155
	CCSD(T)	965*i*	132	337	432	564	2111

	Rotational Constants		
	A_e	B_e	C_e
1	12711	1740	1546
2	15770	1574	1445
3	9452	2230	1827
4	11080	2431	2022

[a] Normal modes intensities (in km/mol) at MP2/aVQZ for all minima in parentheses. Rotational constants (in MHz) at the CCSD(T)/CBS level. Intensities are not available for frequencies below 150 cm^{-1}.

study can be compared with, we shall limit the present discussion to a comparison with data of other species showing similar bonds and structural characteristics.

First of all, we note that the disulfur bridges in the two most stable structures are slightly different. In structure **1**, it can be identified as a normal S−S single bond with a predicted equilibrium distance of 2.014 Å (2.000 and 2.018 Å) obtained at the CCSD(T)/CBS (MP2/CBS and DFT/B3LYP/CBS) levels of calculation, respectively. In structure **2**, it was found to be about 5% shorter, 1.919 Å (1.899 and 1.926 Å), respectively, with the CCSD(T)/CBS (MP2/CBS and DFT/B3LYP/CBS) approaches. For the most stable isomer, the S−S bond distance has an intermediate value between 2.055 Å, found in HSSH,[33] and the one calculated for BrSSBr, 1.959 Å.[20] In the case of the isomer SSHBr, the shorter SS bond distance found, 1.919 Å, can be viewed, in terms of a simple orbital picture, as a dative-type bond with the central sulfur atom donating an electron pair to the terminal sulfur; this bond distance is intermediate that of the single bond in HSSH (2.055 Å) and the double bond in S_2, 1.889 Å.[34] We stress again that an analogue of structure **2**, here described for the first time, was not found in previous studies of the isovalent oxygenated species.

We turn our focus now to the SBr bond distances. For isomers **1** and **2**, our best CCSD(T)/CBS results are 2.215 and 2.327 Å, respectively; with the MP2/CBS and DFT/B3LYP/CBS approaches, we obtained 2.199 Å (**1**), 2.251 Å (**1**), and 2.321 Å (**2**), 2.378 Å (**2**), respectively. For **1**, our best distance is about 3% longer than a typical singly bonded species, as in SBr, for which we found 2.148 Å;[35] for **2**, this elongation amounts to about 8%. This increase in bond distance for **2** can be partially accounted for by a shift in the electron density on the sulfur to make the dative bond with the other sulfur atom. This weakening of the bond strength is also reflected in the vibrational frequency of the SH stretching mode as discussed in the next section. A steric repulsion factor in **2** can be also invoked to rationalize this longer distance. In isomers **3** and **4**, on the other hand, the bromine atom plays the role of electron pair donor: one in **3**, and two in **4**. In **3**, the bromine atom participates both in a covalent bond with a divalent sulfur atom, resulting in a bond distance of 2.287 Å (2.244 Å, MP2/CBS; 2.333 Å, DFT/B3LYP/CBS), and in a dative-type bond with a terminal sulfur atom, with a shorter equilibrium distance of 2.115 Å (2.083 Å, MP2/CBS; 2.130 Å, DFT/B3LYP/CBS), respectively. One should notice that for the two SBr bond lengths in **3** all methods predict the central one to be longer by 7−10%. The central SBr bond distance in **3** is even larger (∼10%) when compared with the one in **1** and again can be rationalized in terms of a decrease in electron density on the bromine atom as a result of the dative bond formation between bromine and the terminal sulfur atom. For the least stable pyramidal isomer **4**, the bromine atom forms two dative-type bonds with the sulfur atoms, with an equilibrium distance of 2.133 Å (2.095, 2.158 Å) predicted by the CCSD(T)/CBS (MP2/CBS, DFT/B3LYP/CBS) methods, respectively. These values are as large as the SBr dative bond distance in **3**. As discussed in the next section, the formation of the two dative-type bonds has a significant effect on the vibrational frequency of the HBr stretching mode as compared to the one in the free molecule.

Concerning the H−S bond distance in **1**, **2**, and **3**, the optimized values predicted at the CCSD(T)/CBS (MP2/CBS, DFT/B3LYP/CBS) levels of theory are 1.345 Å (1.340, 1.350 Å) for **1**, 1.354 Å (1.352, 1.359 Å) for **2**, and 1.342 Å (1.338, 1.344 Å) for **3**, respectively. We note that they are consistent with the HS distance found in HSBr (1.340 Å).[9] Again, we stress that for isomer **2**, in which the central sulfur atom forms a dative-type bond with the terminal sulfur, this distance is slightly longer as a consequence of a charge density migration from the central sulfur atom to the terminal one.

As to the bond angles, with the exception of the ∠HSBr in **3**, 92.8°, very close to the one in H_2S, 92.2°,[33] which can be rationalized in terms of bond formation involving the two $3p_z$-type orbitals in sulfur, the other bond angles ∠HSS (98.9°) and ∠SSBr (105.9°) in **1**, ∠HSS (104.8°) and ∠BrSS (114.2°) in **2**, ∠SBrS (114.0°) in **3**, and ∠HBrS (101.2°) in **4** all somehow reflect electron pair (bonded and nonbonded) interactions with angle values around the one of the ideal electron pair tetrahedron. Concerning the dihedral angle, in **1**, **2**, and **3** it centers around 90°: 86.8° in **1**, 94.7° in **2**, and 81.3° in **3**, but for the case in which the bromine atom forms two dative-type bonds, the dihedral angle is 109.9°.

3.C. Vibrational Frequencies. Concerning the harmonic vibrational frequencies, we note first that, for isomers **1** and **3**, and the transition state **2/3**, in which the sulfur atom has only two covalent bonds, the calculated values of 2653, 2695, and 2725 cm^{-1} are very close to that corresponding to the stretching mode of the SH radical, 2712 cm^{-1}.[34] On the other hand, in isomer **2** and the transition states **1/2** and **1/3**, their corresponding values are about 100 cm^{-1} smaller: 2555, 2585, and 2533 cm^{-1}, respectively. To account for this red shift, one should notice that in **2** there is a decrease in the electron density on the central sulfur atom as a consequence of an electron pair donation and atoms migration in **1/2** and **1/3**. The other ω_{e6} frequencies close to 2100 cm^{-1} are those of the stretching mode of the HBr group, which in the free molecule is equal to 2649 cm^{-1}.[34] In this case, the significant electron density shift from the HBr moiety to account for the two dative-type bonds seems to be the rationale that explains these much lower frequencies.

The frequency associated with the S−S stretching mode equals 532 cm^{-1} in **1**, 609 cm^{-1} in **1/2**, and 656 cm^{-1} in **2**. This trend is compatible with the shortening of the S−S bond distance in this sequence; for comparison, in the free S_2 molecule, ω_e is equal to 726 cm^{-1}. As to the S−Br stretching, we found the values of 388 and 306 cm^{-1} in **1** and **2**, respectively; for the free SBr radical, we have obtained 461 cm^{-1}.[9] In **3**, the SBr stretching mode corresponds to ω_{e4} (477 cm^{-1}) and in **4** to ω_{e2} (383 cm^{-1}) and ω_{e3} (410 cm^{-1}). The lowest frequency in **1** and **2**, respectively, equal to 169 and 148 cm^{-1}, corresponds to the bending mode BrSS, and in **3** and **4**, associated with the SBrS bending mode, we have 129 and 145 cm^{-1}, respectively. The bending mode HSS can be associated with ω_{e5} in **1** and **2**, with frequency values of 909 and 928 cm^{-1}, respectively, and the HSBr bending mode with ω_{e5} in **3** and **4**, 759 and 715 cm^{-1}, respectively. Complementing these data, in Table 2 we have also listed IR intensities computed at the MP2/aVQZ level of theory for the four minima. These values should provide a rough estimate of the relative intensities and hopefully help experimentalists make the proper IR assignments in the case any of these species come to be isolated.

3.D. Performance of DFT/B3LYP and MP2 Relative to CCSD(T). In this section, our major goal is to examine the expected performance of the methods DFT/B3LYP and MP2 relative to CCSD(T) in situations where this latter approach may become computationally very expensive, as might be the case of the natural extension of the present work to polysulfide systems.

As to the energetic results summarized in Table 1, one can notice that both methods DFT/B3LYP and MP2 underestimate the location of isomer **2** by about 10%. As to isomers **3** and **4**, MP2 and DFT/B3LYP have opposite trends: the relative position is overestimated in the MP2 calculations and underestimated with the DFT/B3LYP approach. This discrepancy can be as large as about 5% in **3** and about 3% for MP2 in **4**. For species **4**, both results DFT/B3LYP and CCSD(T) are very close. For the determination of thermodynamic quantities with chemical accuracy, such large errors are clearly unacceptable. When we focus on the localization of the stationary states, we note that the DFT/B3LYP results are usually underestimated, whereas the MP2 values are overestimated, the exception being the transition state **1/2′** for which both heights are underestimated by about 1.3 kcal/mol. One should notice, however, that the MP2 prediction can be in error by about 9% in **2/3**, and by about 4% in **3/4**. As to the barrier height for the isomerization **3** → **4**, the MP2 value is overestimated by about 14% and the DFT/B3LYP one by about 4%. Overall, DFT/B3LYP/CBS performs better than MP2/CBS, but the results obtained with the former method still lack chemical accuracy in general.

The major structural features of the four isomers are predicted correctly by all three methods, but no systematic trend can be established for each method. The central S−S bond distance in **1** and **2** is slightly overestimated in the DFT/B3LYP calculation and slightly underestimated in the MP2 one relative to the CCSD(T) results. For the SBr bond distance, DFT/B3LYP predicts longer distances in all four isomers, the discrepancy being as large as 0.05 Å, whereas with MP2, these distances are usually underestimated, at most by 0.06 Å. Most bond angles and dihedral angles were found to lie within ±1° of each other, as predicted by the different methodologies. In general, MP2 predicts underestimated distances and angles relative to the CCSD(T) results. Also, the DFT/B3LYP angles are in general slightly overestimated.

Finally, concerning the harmonic frequencies shown in Table 2, one can see that MP2 overestimates these values for all four isomers, whereas with the DFT/B3LYP calculation the results are all underestimated relative to the CCSD(T) values, the largest deviation being that for the HBr stretching in **6**, 125 cm^{-1} (DFT/B3LYP). Contrasting with the energetic results, in general, the MP2 frequencies are closer to the CCSD(T) results than those predicted by DFT/B3LYP.

4. Conclusions

This study is the first in the literature to characterize in a systematic way four local minima and five transition states on the [H, S_2, Br] PES using three different approaches: MP2, DFT/B3LYP, and CCSD(T), all at the CBS limit. These molecules are potentially a new route of coupling the sulfur and bromine chemistry in the atmosphere, and conditions of high concentration of H_2S like in volcanic eruptions might contribute to their formation. In comparison with the analogue oxygenated surface, the present one has unique features not present in the latter one. For both surfaces, a skewed HXXBr structure is associated with the global minimum, whereas a pyramidal-like SSHBr structure lying 18.85 kcal/mol above the global minimum was predicted in this study, and a skewed one HOBrO was found at 3.8 kcal/mol for the [H, O_2, Br] surface. In this study, the skewed structure HSBrS was located at 50.29 kcal/mol above the global minimum. Very high in energy, the pyramidal-like structure with two dative SBr bonds ($HBrS_2$) is very likely to isomerize to the most stable species (HSSBr), if it happens to be formed by some reactive channel. Although general geometric and energetic trends for the new species described in this investigation are correctly predicted by the two lower level methods, only CCSD(T) is expected to give reliable thermodynamic quantities within chemical accuracy. Similarly, for the barrier heights of the isomerization reactions, again only the CCSD(T)/CBS results are expected to have the necessary accuracy to allow for the calculation of reliable rate constants.

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References and Notes

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