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Search for Stratospheric Bromine Reservoir Species: Theoretical Study of the Photostability of Mono-, Tri-, and Pentacoordinated Bromine Compounds

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Previous work has shown that pentacoordinated bromine compounds have their lowest excited electronic states shifted to the blue relative to monocoordinated bromine molecules, and that this shift may be large enough to render them photostable in the lower stratosphere. Our earlier work has also shown that certain pentacoordinated bromine compounds are thermodynamically stable relative to their mono- or tricoordinated isomers, suggesting that if a bromine stratospheric reservoir species exists, it may be a pentacoordinated compound. In this study we have examined the singlet and triplet excited electronic states of several bromine compounds, using time dependent density functional theory, to assess their photostability under stratospheric conditions and in order to elucidate the nature of lowest excited states in mono-, tri-, and pentacoordinated bromine molecules. The triplet states have been included due to the strong spin−orbit mixing in bromine. We have found several pentacoordinated bromine/oxygen compounds that could be photostable in the lower stratosphere, but we have also found that monovalent bromine compounds where the bromine atom is bonded to an atom with no lone-pair p-electrons is far and away the most photostable. Attachment/detachment electron density plots have been useful in ascertaining the nature of the excited electronic states and their likely path to photodissociation.

Introduction

It is known that in the Earth's stratosphere the total destruction of ozone due to chlorine and bromine is similar (e.g., see refs 1−8) even though the stratospheric abundance of chlorine is about 100 times greater than for bromine.[8,9] This is due to the fact that a higher percentage of total bromine is in more reactive forms compared to chlorine.[8] It is well established that the main chlorine reservoir species in the stratosphere is HCl with $ClONO_2$ and HOCl being the next most important reservoir compounds. The situation for bromine is much less certain, as it is also established that the destruction rates for HBr and $BrONO_2$ are much faster[8] relative to their chlorine analogues. Experiments have shown that in sunlight conditions $BrONO_2$ is readily destroyed through photolysis in the lower stratosphere[10] while under dark conditions $BrONO_2$ is destroyed through heterogeneous reactions.[11,12] The bond energy for HBr is 15.5 kcal/mol weaker than that for HCl, making HBr more susceptible to radical attack, thermal dissociation, and heterogeneous reactions,[13] even though it is photostable in the lower stratosphere.[14] Indeed, the rate of reaction for OH + HBr is a full 2 orders of magnitude larger than that for OH + HCl.[14] The other Br compounds most commonly discussed in the literature as possible minor reservoir species, HOBr and BrCl, are also readily photolyzed in the lower stratosphere.[10,14] However, there is evidence that other Br reservoir species may exist since the total stratospheric Br concentration is larger than can be explained by current models[15] (see also ref 16 for a discussion on possible bromine reservoir species outside of Cl analogues).

Thus, it is evident that if other Br stratospheric reservoir compounds exist, they will not be simply Cl analogues since the relevant Br compounds are much more easily destroyed through photolysis, gas-phase reaction with OH, and/or heterogeneous reactions. In this regard, we recently showed that hypercoordinated bromine compounds, specifically pentavalent compounds, can be photostable in the lower stratosphere since their lowest excited singlet electronic state shifts to the blue relative to monovalent bromine compounds[17] and may be centered above 4.31 eV. This is important since solar radiation that reaches the lower stratosphere is cut off near 4.31 eV or 288 nm.[14] Further, an analysis of bromine/oxygen bonding has shown that hypercoordinated bromine compounds, specifically those that are pentacoordinated, exhibit thermodynamic stability provided the bonding partners are strongly electronegative, and in fact they are often the most stable isomers.[18] This is in contrast to the chlorine/oxygen hypercoordinated compounds, where the normal single-valent isomer is usually the most stable.[18] In addition, it was found that while Br−O single bonds are usually about 7 kcal/mol weaker than their Cl−O analogues, Br═O multiple bonds are often stronger than their Cl═O analogues.[18] The bonding in these hypercoordinated compounds is comprised of a mixture of ionic and hypervalent p → d covalent bonding, with the ionic component being dominant, which explains why the bromine/oxygen multiple bonds are often stronger than their chlorine analogues since bromine is more easily ionized than chlorine.

In our previous study,[17] we also showed that the lowest excited triplet state of the pentavalent bromine compounds may

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TABLE 1: Comparison of TDDFT versus LRCCSD Results for Singlet Excitations (eV)[a]

HOBr			HBrO			HOBrO			$HBrO_2$		
state	LRCCSD	TDDFT	state	LRCCSD	TDDFT	state	LRCCSD	TDDFT	state	LRCCSD	TDDFT
$1^1A''$	3.58	3.22	$1^1A''$	3.29	3.06	1^1A	2.82	2.51	$1^1A'$	4.74	4.51
$1^1A'$	4.44	4.08	$2^1A''$	4.19	3.92	2^1A	4.25	4.06	$1^1A''$	5.42	5.12
$2^1A''$	6.45	6.09	$1^1A'$	4.37	3.96	3^1A	5.26	5.05	$2^1A'$	5.65	5.24
$3^1A''$	6.85	6.26	$2^1A'$	5.58	5.25	4^1A	5.53	5.21	$2^1A''$	5.68	5.36

[a] The TZ2P(sp2) basis set used previously for the LRCCSD was used for all calculations. See text for details.

occur in a region accessible by the Sun's actinic flux,[14] which means that this state may be the most likely photodissociation pathway. This, of course, depends on the efficiency of spin−orbit coupling in transferring oscillator strength to the singlet−triplet transition. In this regard, we note that Peterson et al.[19] have recently shown that the spin−orbit coupling is significant enough in $BrONO_2$ to suggest that singlet−triplet excitations are most important for photodissociation in the Earth's stratosphere.

We note that by photostable we mean that the compound cannot photodissociate due to the excited electronic states being inaccessible to the available radiation from the Sun's actinic flux. It is certainly the case that even if electronic states are accessible, a compound can exhibit a measurable lifetime if the oscillator strength is small, but under lit conditions it will eventually photodissociate, and thus it will not be a long-lived reservoir species.

The purpose of the present study is to examine the electronic spectroscopy of possible bromine stratospheric reservoir species, including several singlet and triplet states, to determine whether there are any compounds that will not readily photodissociate in the lower stratosphere. We have included several monovalent bromine compounds, such as HOBr and $BrONO_2$, to compare with experiment and to assess, using electron attachment/detachment densities,[20] the nature of the excited states. In fact, we will use electron attachment/detachment densities extensively to assess whether a particular excited electronic state is likely to lead to dissociation, and if so along which bond. We also reexamine some mono-, tri-, and pentavalent compounds, specifically HOBr, HBrO, HOBrO, and $HBrO_2$, to benchmark time-dependent density functional theory (TDDFT) against the more advanced methods used previously.[17] Our main focus, however, is to examine pentavalent bromine compounds that possess several electronegative moieties bonded to the bromine atom, such as O_2BrONO_2 which has been shown to be thermodynamically very stable,[16] that have the potential to be photostable in the lower stratosphere. The additional pentavalent bromine molecules included in the present study are $HOBrO_2$, $FBrO_2$, $(HO)_3BrO$, F_3BrO, CF_3OBrO_2, and CF_3BrO_2. In addition, since HBr is photostable in the lower stratosphere, we have also examined some monovalent Br compounds in order to determine the characteristics of a monovalent Br compound that make it photostable. Additional monovalent compounds included in the present study include FBr, CF_3Br, and CF_3OBr. For completeness, the following tricoordinated compounds have also been investigated: $(HO)_3BrO$, F_3BrO, CF_3BrO, and CF_3OBrO. It is our goal to determine whether any of the compounds investigated here may be considered photostable in the Earth's lower stratosphere and thus may possibly be stratospheric Br reservoir species.

The theoretical approach is detailed in the next section followed by results and discussion. The final section contains our conclusions.

Theoretical Approach

The geometrical structures have been optimized using the 6-31+G(2df) basis set in conjunction with the B3LYP density functional theory (DFT) approach.[21] Where available, these structures agree well with previous theoretical calculations and experiment. The detailed structures are available as Supporting Information. Vertical electronic excitation energies have been computed using the time dependent density functional theory (TDDFT) method[22] using the B3LYP functional. As mentioned in the Introduction, this approach has been benchmarked against the more rigorous linear response singles and doubles coupled-cluster (LRCCSD) method for a subset of the molecules investigated here. For the TDDFT calculations, the 6-31+G(2df) basis set has been used, except for the benchmark studies where the TZ2P(sp2) basis set (triple-ζ, double polarized plus two sets of diffuse s and p functions) used previously for the LRCCSD calculations was utilized.[17]

Characterization of the excited states has been aided by the use of attachment/detachment density plots. The attachment/detachment densities have been computed according to the approach developed by Head-Gordon et al.,[20] with the plotted surfaces representing containment of approximately 90% of the attachment or detachment density. Before discussing the attachment/detachment densities below, a simple explanation of attachment and detachment densities is warranted. For an excitation completely dominated by a highest occupied molecular orbital (HOMO) transition into the lowest unoccupied molecular orbital (LUMO), then the detachment density would correspond to the HOMO and the attachment density would correspond to the LUMO. The attachment/detachment densities, however, have the advantage that they are not limited to a single orbital transition, but in fact capture this information for the entire excitation no matter how many orbitals are involved. In other words, the detachment density corresponds to the electron density that is present in the ground electronic state but is missing in the excited electronic state, and the attachment density corresponds to the electron density present in the excited electronic state but missing in the ground electronic state. Hence it is clear that for a vertical electronic excitation, attachment and detachment densities integrated over all space must exactly cancel.

All calculations were performed with the Q-Chem 2.1 quantum chemistry program package.[23]

Results and Discussion

A. Benchmarking TDDFT. We first benchmark TDDFT versus coupled-cluster methods for HOBr, HBrO, HOBrO, and $HBrO_2$. Table 1 presents a comparison of TDDFT and LRCCSD results for singlet vertical excitation energies (VEEs) while Table 2 presents a comparison of TDDFT with direct state calculations at the CCSD(T) and B3LYP level for the triplet VEEs. The coupled-cluster results were taken from our previous study.[17] In both tables, the VEEs are reported in eV relative to the singlet ground state. The coupled-cluster results should be the most

TABLE 2: Comparison of Excitation Energies (eV) for the Lowest Triplet State of Each Symmetry[a,b]

	$1^3A'$			$1^3A''$		
molecule	CCSD(T)	B3LYP	TDDFT	CCSD(T)	B3LYP	TDDFT
HOBr	3.56	3.37	3.11	2.77	2.46	2.30
HBrO	3.32	3.14	2.97	2.45	2.22	2.07
HOBrO	2.25	1.93	1.85			
$HBrO_2$	4.15	3.75	3.62	4.92	4.72	4.50

[a] See text for a more complete discussion. [b] The TZ2P(sp2) basis set used previously for the LRCCSD was used for all calculations. See text for details.

reliable for both the singlet and triplet VEEs. Note that for the triplet VEEs the direct calculation approach is particularly reliable since it approximately includes the effects of connected triple excitations. For the singlet VEEs, the lowest four excited singlet states have been included for each molecule. For the triplet VEEs, we intended to include the lowest triplet from each unique symmetry irreducible representation, which means A′ and A″ states for HOBr, HBrO, and $HBrO_2$, and an A state for HOBrO; however, the CCSD(T) result for the $^3A''$ state of $HBrO_2$ from ref 17 was for a higher-lying state accessible due to the orbital occupations used. All of the other triplet states included in Table 2 represent the lowest state of the given symmetry.

Examination of the VEEs in Table 1 shows that the TDDFT results for singlet states are consistently lower than the corresponding LRCCSD value. This underestimate is generally around 0.2−0.4 eV, although for the highest state of HOBr the underestimate is larger, almost 0.6 eV. The fact that TDDFT underestimates LRCCSD so consistently, even across changing bromine coordination numbers, suggests that TDDFT should be a reliable method for the study of the VEEs for the bromine compounds of interest in this study.

Comparison of the CCSD(T) and TDDFT VEEs listed in Table 2 shows again that TDDFT is an underestimate. In this case, TDDFT is consistently around 0.3−0.5 eV lower than the CCSD(T) value. While this is slightly larger than the difference found for the singlet states, we note that these differences are not directly comparable since different coupled-cluster approaches were used for the benchmarks. However, it is important that the difference between TDDFT and CCSD(T) is consistent in both cases, since this indicates that TDDFT is a reasonable approach for estimation of triplet state VEEs for the bromine compounds included in the present study.

We included the B3LYP direct calculations for the triplet states (Table 2) to see how this approach would perform. It is interesting that the direct B3LYP VEEs are always between the CCSD(T) and TDDFT values. The limited results we have in Table 2 suggest that B3LYP used in this fashion should lead to fairly consistent errors and errors generally smaller than TDDFT. Of course, direct B3LYP calculations are not practical for higher lying states of the same symmetry (unless the orbital occupations are unique).

The benchmark studies presented in Tables 1 and 2 clearly show that while the TDDFT approach underestimates VEEs by between 0.2 to 0.5 eV for the different types of bromine compounds (i.e., different coordination numbers), this error is consistent and thus TDDFT is a useful technique to study a broad range of bromine compounds. The results presented in Tables 1 and 2 also confirm our earlier observations[17] that pentacoordinated bromine/oxygen compounds have their VEEs significantly blue shifted relative to monovalent bromine/oxygen compounds. In the following sections, we examine the TDDFT VEEs for the monovalent, tricoordinated, and pentacoordinated bromine compounds, respectively, using the 6-31+G(2df) basis set.

TABLE 3: TDDFT VEEs (eV) for the Monovalent Bromine/Oxygen Compounds

HOBr			$BrONO_2$			CF_3OBr		
state	VEE	f[a]	state	VEE	f[a]	state	VEE	f[a]
$1^1A''$	3.29	0.0000	$1^1A''$	3.45	0.0002	$1^1A''$	3.44	0.0000
$1^1A'$	4.20	0.0021	$1^1A'$	4.02	0.0012	$1^1A'$	4.08	0.0015
$2^1A''$	6.09	0.0051	$2^1A''$	4.84	0.0000	$2^1A''$	6.06	0.0016
$3^1A''$	7.80	0.0005	$2^1A'$	4.97	0.0075	$2^1A'$	7.15	0.0407
$1^3A''$	2.34		$1^3A''$	2.54		$1^3A''$	2.49	
$1^3A'$	3.22		$1^3A'$	3.13		$1^3A'$	3.08	
$2^3A''$	5.16		$2^3A'$	4.08		$2^3A''$	5.26	
$2^3A'$	5.63		$2^3A''$	4.31		$2^3A'$	5.62	

[a] Oscillator strength for singlet states. The 6-31+G(2df) basis set was used. See text for details.

The 6-31+G(2df) basis used for most of the calculations in the present study is a more complete basis set than the TZ2P-(sp2) basis used in our benchmark LRCCSD study,[17] especially for the hypercoordinated Br/O compounds. This is due to the inclusion of *f* functions on the non-hydrogen atoms, especially bromine. Comparison of the TDDFT results for the four molecules included in this benchmark section for the TZ2P-(sp2) and 6-31+G(2df) basis sets (see Tables 1 through 4) shows good agreement for all but one of the singlet states of HOBr, with the agreement deteriorating as the Br coordination increases. For the hypercoordinated compounds, whenever the difference is larger than 0.15 eV, the TDDFT VEE with the 6-31+G(2df) basis set is at lower energy, indicating that the TZ2P(sp2) basis set is lacking in high angular momentum functions. Hence, while TDDFT is a reasonable approach to study VEEs in hypercoordinated Br/O compounds as concluded from comparison to LRCCSD, it is clear that the one-particle basis set must include appropriate diffuse and high angular momentum functions.

B. Monovalent Br/O Compounds. TDDFT VEEs for the monovalent bromine/oxygen compounds, HOBr, BrONO2, and CF_3OBr, are presented in Table 3. For all of the remaining compounds we have included the lowest four singlet and triplet TDDFT excitation energies as well as the computed oscillator strength, *f*, for the singlet states. As can be seen from examination of Table 3, all of these compounds have at least one singlet state and two triplet states accessible by the solar actinic flux cut off of 4.31 eV, even taking into account that the TDDFT excitation energy will be underestimated by 0.2 to 0.5 eV. The TDDFT VEEs reported here are consistent with previous theoretical and experimental studies (for example, see refs 17, 24−27), and more importantly, with previous assessments on the photostability of HOBr and $BrONO_2$ in the lower stratosphere. It is clear that all of these monovalent Br/O compounds will readily photodissociate in the lower stratosphere due to these low-lying states. We note that it is important to consider the triplet states as well since bromine has a large spin−orbit coupling, and therefore triplet states from bromine compounds will often have a nonnegligible intensity (for example, see ref 19 where it is concluded that for bromine nitrate, $BrONO_2$, most of the photodissociation in the lower stratosphere is due to excitation into a triplet state).

It is possible to gain insight into the nature of low-lying excitations in monovalent Br/O compounds by examination of the attachment/detachment density plots for the various species. As an example of an attachment/detachment plot for a monovalent Br/O compound, we present the attachment/detachment

TABLE 4: TDDFT VEEs (eV) for the Tricoordinated Bromine/Oxygen Compounds

HBrO			HOBrO			CF_3BrO			CF_3OBrO		
state	VEE	f[a]	state	VEE	f[a]	state	VEE	f[a]	state	VEE	f[a]
$1^1A''$	3.00	0.0009	1^1A	2.36	0.0001	$1^1A''$	3.15	0.0008	1^1A	1.89	0.0001
$2^1A''$	3.60	0.0003	2^1A	4.12	0.0007	$2^1A''$	3.43	0.0002	2^1A	4.16	0.0004
$1^1A'$	3.81	0.0059	3^1A	4.75	0.0042	$1^1A'$	4.04	0.0046	3^1A	4.44	0.0015
$2^1A'$	5.19	0.0578	4^1A	5.04	0.0798	$2^1A'$	5.16	0.0819	4^1A	4.90	0.1184
$1^3A''$	1.83		1^3A	1.71		$1^3A''$	2.08		1^3A	1.18	
$1^3A'$	2.68		2^3A	2.45		$1^3A'$	3.00		2^3A	1.99	
$2^3A''$	3.33		3^3A	3.17		$2^3A''$	3.05		3^3A	3.20	
$2^3A'$	3.69		4^3A	3.85		$2^3A'$	3.39		4^3A	3.69	

[a] Oscillator strength for singlet states. The 6-31+G(2df) basis set was used. See text for details.

Figure 1. Pictured is the detachment (red) and attachment (blue) electron density for the first excited singlet state of $BrONO_2$. The Br atom is purple, the O atoms are red, and the N atom is blue. See text for details on the plots.

Figure 2. Pictured is the detachment (red) and attachment (blue) electron density for the first excited singlet state of HOBrO. The Br atom is purple, the O atoms are red, and the H atom is white. See text for details on the plots.

density plot for the lowest excited singlet state of $BrONO_2$ in Figure 1. Examination of Figure 1 shows that the detachment density is a mixture of out-of-plane Br and O lone-pair p-electrons; that is the O atom that is bonded directly to Br. Note also that the largest contribution to the detachment density arises from the Br lone-pair p-electrons. One important point is that in all the Br/O monovalent compounds studied here, there is clearly a mixing of the lone-pair p-electrons and orbitals between the Br atom and the O atom to which it is directly bonded, and it is also important to note that the detachment density arises mainly from the lone-pair p-electrons on the Br. In subsequent sections, it will be seen that the nature of the detachment density is significantly altered depending on the Br coordination number.

The attachment density shows that the excited-state density is placed in a Br−O antibonding molecular orbital. This suggests that excitation into the lowest excited singlet state will lead to dissociation of the Br−O single bond. We shall see that this is prevalent in the tri- and pentacoordinated Br/O compounds as well.

Experimental VEEs[24−27] are available for the lowest two excited singlet states (3.54 eV and 4.35−4.43 eV) and the lowest triplet state of HOBr (2.71−2.82 eV). Consistent with our earlier study[17] and the previous LRCCSD benchmark section, agreement between TDDFT and experiment is reasonable with TDDFT underestimating experiment by between 0.2 to 0.5 eV. The comparison between experiment and TDDFT is further support for our assertion that TDDFT is consistently low by between 0.2 to 0.5 eV and because of this consistency, it is a reasonable approach for the present study.

It is also noteworthy that Peterson et al.[19] have computed LRCCSD VEEs for $BrONO_2$, and our TDDFT values are in good agreement with these, again being somewhat too low, with one exception. Our lowest four triplet states correspond well with their LRCCSD calculations, but for the singlet states we see correspondence for only the three lowest states. It appears that they may have missed the state that we have labeled $2^1A'$. In any case, the agreement with the other seven states is entirely consistent with our own LRCCSD benchmark studies.

C. Tricoordinated Br/O Compounds. TDDFT VEEs for the tricoordinated bromine/oxygen compounds included in the present study, HBrO, HOBrO, CF_3BrO, and CF_3OBrO, are presented in Table 4. Examination of Table 4 shows immediately that tricoordinated bromine/oxygen compounds possess several low lying electronic states, both singlet and triplet, that are susceptible to photodissociation from the actinic solar flux below 4.31 eV. This is consistent with the fact that their thermal stability is significantly lower than that for either monovalent or pentacoordinated Br/O compounds.[18] In our model of Br/O hypercoordination,[18] we assert that the tricoordinated species possess a mixture of ionic and covalent bonding with the covalent component involving promotion of a lone-pair Br p-electron into an empty low-lying d-orbital and formation of hybrid p−d molecular orbitals. This model suggests that the tricoordinated species should be thermally less stable than either the monovalent or pentacoordinated species, and that the tricoordinated species should possess lower-lying electronic states than either the monovalent or pentacoordinated species, which in fact is observed. While the ionic component of the bonding is larger, the covalent component is significant enough to impact the stability of the tricoordinated and pentacoordinated molecules. In summary, the results presented in Table 4 suggest that any tricoordinated Br/O compounds will not be photostable in the lower stratosphere.

It is instructive to examine the attachment/detachment plot for a representative tricoordinated Br/O compound as shown in Figure 2 for HOBrO. Examination of Figure 2 shows that, similar to the case for the monovalent Br/O compounds, the detachment density is a mixture of Br and O lone-pair p-electrons, but in this case it is from the O atom that is doubly bonded to the Br atom which, of course, is not present in the monovalent Br/O molecule. Another significant difference from the monovalent case is the fact that there is a much more equal contribution from the Br and O atoms in the detachment density. Hence the detachment density suggests that there is increased mixing between the Br and O lone-pair p-electrons (for the doubly bonded O atom) relative to the monovalent case.

The attachment density also shows some difference between the monovalent and tricoordinated species. The attachment density in Figure 2 is into an antibonding Br−O molecular orbital, but it is into an antibonding orbital for the single Br−O bond. This suggests that excitation into the lowest singlet state will lead to dissociation of the Br−O single bond.

TABLE 5: TDDFT VEEs (eV) for Some of the Pentacoordinated Bromine/Oxygen Compounds

$HBrO_2$			O_2BrONO_2			$HOBrO_2$			$(OH)_3BrO$		
state	VEE	f^a	state	VEE	f^a	state	VEE	f^a	state	VEE	f^a
$1^1A'$	4.33	0.0141	1^1A	3.22	0.0145	1^1A	4.28	0.0038	1^1A	4.20	0.0013
$1^1A''$	4.71	0.0024	2^1A	3.39	0.0070	2^1A	4.36	0.0088	2^1A	4.30	0.0070
$2^1A'$	4.85	0.0116	3^1A	3.48	0.0240	3^1A	4.78	0.0063	3^1A	4.64	0.0050
$2^1A''$	5.12	0.0001	4^1A	3.76	0.0015	4^1A	5.51	0.0034	4^1A	4.93	0.0032
$1^3A'$	3.07		1^3A	1.67		1^3A	3.13		1^3A	3.47	
$2^3A'$	3.91		2^3A	2.57		2^3A	3.49		2^3A	3.72	
$1^3A''$	3.93		3^3A	2.89		3^3A	4.09		3^3A	3.99	
$2^3A''$	4.25		4^3A	3.02		4^3A	4.23		4^3A	4.07	

[a] Oscillator strength for singlet states. The 6-31+G(2df) basis set was used. See text for details.

TABLE 6: TDDFT VEEs (eV) for Some of the Pentacoordinated Bromine/Oxygen Compounds

$FBrO_2$			F_3BrO			CF_3BrO_2			CF_3OBrO_2		
state	VEE	f^a	state	VEE	f^a	state	VEE	f^a	state	VEE	f^a
$1^1A'$	3.94	0.0062	1^1A	4.08	0.0002	$1^1A'$	4.23	0.0229	1^1A	3.61	0.0081
$1^1A''$	3.98	0.0004	2^1A	4.54	0.0107	$1^1A''$	4.49	0.0011	2^1A	3.69	0.0056
$2^1A''$	4.86	0.0176	3^1A	5.15	0.0045	$2^1A'$	4.80	0.0035	3^1A	3.96	0.0022
$2^1A'$	5.59	0.0036	4^1A	5.32	0.0041	$2^1A''$	5.02	0.0050	4^1A	4.75	0.0177
$1^3A'$	2.93		1^3A	3.20		$1^3A'$	2.68		1^3A	2.28	
$1^3A''$	3.14		2^3A	3.69		$1^3A''$	3.90		2^3A	2.87	
$2^3A''$	3.61		3^3A	4.41		$2^3A'$	3.95		3^3A	3.29	
$2^3A'$	3.99		4^3A	4.48		$2^3A''$	4.28		4^3A	3.41	

[a] Oscillator strength for singlet states. The 6-31+G(2df) basis set was used. See text for details.

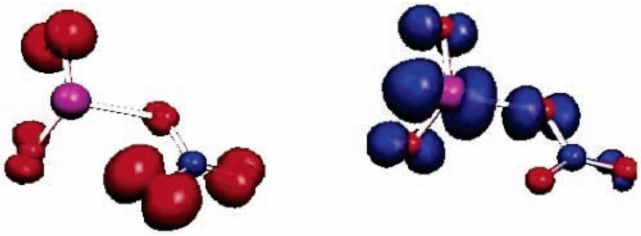

Figure 3. Pictured is the detachment (red) and attachment (blue) electron density for the first excited singlet state of O_2BrONO_2. The Br atom is purple, the O atoms are red, and the N atom is blue. See text for details on the plots.

D. Pentacoordinated Br/O Compounds. TDDFT VEEs for the pentacoordinated bromine/oxygen compounds $HBrO_2$, O_2BrONO_2, $HOBrO_2$, $(HO)_3BrO$, $FBrO_2$, F_3BrO, CF_3BrO_2, and CF_3OBrO_2, are presented in Tables 5 and 6. As detailed in the Introduction, pentacoordinated Br/O compounds were a focus of the present study, and examination of Tables 5 and 6 shows that there are indeed several pentacoordinated Br/O compounds whose VEEs have shifted considerably to the blue. One compound of particular interest, as a possible reservoir species, in a previous study was O_2BrONO_2.[16] Examination of the VEEs for this compound (Table 5), however, shows that it has several singlet and triplet states below 4.31 eV, even taking into account the 0.2−0.5 eV underestimate of TDDFT VEEs. Figure 3 shows the attachment/detachment density plot for the lowest excited singlet state for O_2BrONO_2, and from this it is evident that the detachment density for this excitation is spread out over both the BrO_2 and NO_2 chromophores. As will be shown later, the detachment density from the BrO_2 chromophore is consistent with the detachment density for the other pentacoordinated Br compounds studied here. That is, the detachment density is entirely from the lone-pair p-electrons of the elements bonded to the Br and unlike the monovalent or tricoordinated cases, the Br atom does not contribute to the detachment density. For O_2BrONO_2, it appears that any blue-shift which may have occurred due to a pentacoordinated bromine atom has been significantly modified by a mixing of the BrO_2 and NO_2 chromphores.

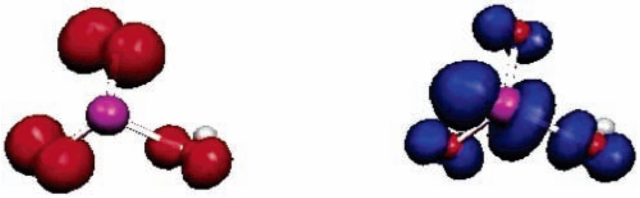

Figure 4. Pictured is the detachment (red) and attachment (blue) electron density for the first excited singlet state of $HOBrO_2$. The Br atom is purple, the O atoms are red, and the H atom is white. See text for details on the plots.

Closer examination of Tables 5 and 6 reveals several pentacoordinated Br/O compounds that could potentially act as stratospheric bromine reservoir species. Specifically, the lowest singlet excited states of $HBrO_2$, $HOBrO_2$, $(OH)_3BrO$, and CF_3BrO_2 are all likely to be inaccessible by the solar actinic flux taking into consideration that the TDDFT VEEs are under estimated by at least 0.3 eV. It is possible that both $FBrO_2$ and F_3BrO are inaccessible as well if the TDDFT VEE is underestimated by 0.5 eV. We note, however, that all of these compounds possess at least one, and in most cases two or more, triplet states that will be accessible by the solar actinic flux, and of course the importance of these states will depend on the efficiency of spin−orbit coupling for these pentacoordinated compounds. To our knowledge, a study of spin−orbit coupling for pentacoordinated bromine compounds has not yet been undertaken.

The attachment/detachment density plots for $HBrO_2$, $HOBrO_2$, $(OH)_3BrO$, and CF_3BrO_2 are similar, so we include the attachment/detachment density plot for $HOBrO_2$ as an example in Figure 4. The first thing to note, as alluded to above, is that the detachment density shows no contribution from the Br atom whatsoever. This is consistent with our assertion that the pentacoordinated Br/O compounds possess no lone-pair p-electrons on the Br atom. Instead, the detachment density is a mixture of lone-pair p-electrons on the various O atoms, with the two doubly bonded O atoms contributing slightly more than the singly bonded O atom. Figure 4 suggests that the main reason that the lowest excited states for pentacoordinated Br/O

TABLE 7: TDDFT VEEs (eV) for Monovalent Bromine Compounds

HBr			FBr			CF_3Br		
state	VEE	f^a	state	VEE	f^a	state	VEE	f^a
$1^1\Pi$	6.67	0.0008	$1^1\Pi$	3.30	0.0004	1^1E	6.37	0.0005
$1^1\Sigma$	12.88	1.2774	$2^1\Pi$	6.83	0.0059	2^1E	8.34	0.0945
$1^3\Pi$	5.96		$1^3\Pi$	2.27		1^3E	5.58	
$1^3\Sigma$	8.45		$2^3\Pi$	5.90		1^3A_1	7.28	

[a] Oscillator strength for singlet states. The 6-31+G(2df) basis set was used. See text for details.

Figure 5. Pictured is the detachment (red) and attachment (blue) electron density for the first excited singlet state of HBr. The Br atom is purple and the H atom is white. See text for details on the plots.

compounds are blue-shifted relative to their monovalent or tricoordinated counterparts is that there is no longer any Br lone-pair p-electron contribution to the detachment density.

Similar to the Figure 2 for the tricoordinated Br/O compound, the attachment density in Figure 4 is into a Br−O antibonding orbital for the Br−O single bond, again suggesting that excitation into the lowest singlet state leads to dissociation of the Br−O single bond. Another interesting feature arises from comparison of the attachment densities in Figures 3 and 4. It appears that the LUMO for these two compounds is very similar, and it also suggests that the main reason for the difference in the VEEs between O_2BrONO_2 and the other pentacoordinated molecules resides in the detachment density or HOMO.

E. Additional Monovalent Br Compounds. It is well-known that HBr does not photodissociate in the lower stratosphere, and thus we decided to include some additional monovalent bromine compounds in order to understand why HBr is different. Therefore we have included TDDFT VEEs for HBr, FBr, and CF_3Br in Table 7. Examination of the results in Table 7 shows that both HBr and CF_3Br will have no singlet nor triplet states accessible by the solar actinic flux, but that FBr has both singlet and triplet states that will be accessible. An examination of the attachment/detachment density plots for the lowest singlet excited states provides some insight to this situation. The attachment/detachment plot for FBr is similar to that for the monovalent Br/O compounds (e.g., Figure 1) in that the detachment density involves a mixture of the Br and F lone-pair p-electrons, whereas for both HBr and CF_3Br the detachment density involves only the Br lone-pair p-electrons. This is demonstrated in Figure 5, the attachment/detachment density plot for the lowest excited singlet state of HBr. The attachment density in Figure 5 goes into a H−Br antibonding orbital, similar to that for all of the Br/O compounds, and similar to that for FBr and CF_3Br. This suggests that the main difference between the HBr and FBr VEEs is due to the HOMO (detachment densities), which also implies that the ionization energy of FBr should be less than that for HBr. This, in fact is not the case according to the NIST Chemistry WebBook.[28] If the difference between the FBr and HBr VEEs resides mainly in the LUMO space, then we would expect the electron affinity of FBr to be larger than that for HBr, which seems reasonable. Applying this analysis to the difference between the FBr and CF_3Br VEEs, however, shows that the situation is more complicated than allowed for by the qualitative arguments used here. For example, one would expect that when adding an electron to CF_3Br, the majority of the additional electron charge would exist on the F atoms, but the attachment density for the lowest excited singlet state of CF_3Br shows very little F character, and mainly C−Br antibonding character, similar to all of the other compounds studied here.

While the attachment/detachment densities may not lead to a definitive explanation as to why compounds such as HBr and CF_3Br possess VEEs inaccessible to the solar actinic flux, we note that a unique difference between these compounds and all of the others included in the present study is that the Br atom is not bonded to an atom possessing lone-pair electrons which have the ability to interact with the Br lone-pair p-electrons. This suggests that, from a photostability perspective, the best bromine reservoir species would be a monovalent bromine compound where the bromine is bonded to an atom with no lone-pair electrons similar to HBr or CF_3Br.

Conclusions

The motivation for this study was to examine the photostability of monovalent, tricoordinated, and pentacoordinated bromine compounds that may be present in the Earth's lower stratosphere in order to determine whether any such compounds could potentially be a stratospheric reservoir species for Br. Our focus was on Br/O compounds because this type of compound is prevalent in the highly oxidizing environment of the lower stratosphere. We have shown beyond doubt that the only type of Br/O compound (that is, where there is a Br−O bond of some type) that may potentially be photostable in the lower stratosphere is a pentacoordinated Br/O compound since their VEEs are blue-shifted relative to monovalent or tricoordinated Br/O compounds. Several pentacoordinated Br/O compounds have been shown to have singlet excited states that are blue-shifted enough as to be inaccessible by the solar actinic flux in the lower stratosphere, including $HBrO_2$, $HOBrO_2$, $(OH)_3BrO$, and CF_3BrO_2. Further, the lowest excited singlet state of $FBrO_2$ and F_3BrO also may be inaccessible to the solar actinic flux, depending on exactly how much TDDFT has underestimated the VEE. However, each of these pentacoordinated compounds will possess at least one, and in many cases two, triplet excited states that will be accessible by the solar actinic flux. Given the prevalence of spin−orbit mixing in bromine compounds, this may be enough to render these compounds unstable to photodissociation, but further work is needed.

We have also examined the VEEs of HBr, FBr, and CF_3Br in an attempt to understand why HBr is photostable in the lower stratosphere, and whether we could find another monovalent compound that is photostable in the lower stratosphere. Our TDDFT results suggests that when Br is bonded directly to another atom with lone-pair p-electrons, the mixing of these lone-pair shells leads to VEEs that are red-shifted and hence accessible to the solar actinic flux. Thus monovalent bromine compounds, where the bromine is bonded to an atom with no lone-pair p-electrons, are far and away the most photostable in the Earth's lower stratosphere. Neither excited singlet nor excited triplet states are accessible to the solar actinic flux for these compounds. The problem, of course, is that many of these bromine compounds tend to be destroyed by other mechanisms, such as H abstraction by OH radical for HBr. Another potential problem is to determine likely formation mechanisms, such as for CF_3Br. While we show that it is photostable, it is unlikely to form from CF_3 + Br since CF_3 readily reacts with O_2,[29] a much more prevalent species than Br. Thus, the present study has shown the types of bromine compounds that will be photostable in the lower stratosphere, but other aspects such as thermal stability, stability with respect to heterogeneous reactions, and possible formation mechanisms will also need to be considered before finally concluding that a particular compound is a likely bromine stratospheric reservoir species.

It is important to note that the attachment/detachment electron density plots were extremely useful in assessing the nature of the excited states and in assessing the nature of the chromophores from which the electronic excitation occurs. In particular, the detachment density is useful in gaining insight into the electronic structure of the ground state, while the attachment density is useful in assessing what will happen to the molecule upon photoexcitation.

Finally, we note that after submission of our paper an interesting analysis by Salawitch et al. on Br in the upper troposphere/lower stratosphere (UT/LS) appeared.[30] They report that the amount of bromine in this region is 4−8 parts per trillion (ppt) greater than previously assumed, and that ozone depletion due to bromine is thus greater than previously calculated. They also point out that the total bromine in this region exceeds the known sources of atmospheric bromine and suggest that numerous very short-lived organic bromine species are the missing source. It is evident from their study that a full understanding of atmospheric bromine has yet to be attained, but also that this is an important topic since bromine is a significant factor in ozone depletion in the lower stratosphere.

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Supporting Information Available: Additional computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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