Ab Initio Study of Bromine Dioxides OBrO and BrOO

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Bromine dioxides OBrO and BrOO are theoretically studied by means of valence-only *ab initio* correlated calculations using TZ(2df) basis sets generated for O, Cl, and Br atoms, especially optimized for averaged relativistic effective core potentials (AREP). Equilibrium geometries for these dioxides are obtained using UMP2 and CCSD(T) electron correlation methods, while harmonic frequencies and dipole moments are computed at the UMP2/AREP/TZ(2df) level. The effect of spin contamination on UMP2 results for geometries and frequencies in these doublet radicals is also discussed. All the analyses dealing with energies are based on CCSD and CCSD(T) calculations. The energetic ordering of both bromine dioxides as well as the two possible dissociation channels, Br + O_2 and BrO + O, are discussed. The nature of the bonding in the energetically more stable BrOO isomer is also investigated by studying its energy surface; a small barrier between 1.2 and 1.7 kcal/mol for this dioxide dissociating into Br + O_2 is predicted.

Introduction

The role of chlorine oxides in various pathways leading to net ozone loss in stratospheric processes is currently a well-established topic.[1,2] Although it was suggested some years ago that bromine compounds were also involved in such processes,[3] bromine oxides have attracted increasing interest only in recent years.[4,5] Nevertheless, the number of studies dealing with bromine molecules of atmospheric interest is still considerably lower than those analyzing chlorine compounds. From a theoretical point of view, this situation is easy to understand insofar as the presence of a heavy atom like bromine poses higher computational demands when performing systematic correlated calculations. The recent work by Lee[6] characterizing triatomic bromine compounds at the CCSD(T)/TZ2P level is one of the first high-level *ab initio* studies in this context.

However, to the best of our knowledge, bromine dioxides OBrO and BrOO have not been studied yet in *ab initio* high-level correlated calculations. The experimental characterization of bromine dioxides is also far from complete, and spectroscopic, thermodynamic, or kinetic studies dealing with bromine dioxides systems are scarce. This situation contrasts with that of the analogous chlorine dioxides OClO and ClOO, thoroughly investigated both experimentally[7,8] and theoretically[9,10] in past years because of their atmospheric role. It has been determined that the unsymmetrical ClOO isomer is thermodynamically more stable than OClO by about 4 kcal/mol[10] but is kinetically unstable and quickly dissociates into atomic chlorine and molecular oxygen.[11] Regarding bromine dioxides, OBrO is known to be much less stable than OClO, and before 1990 it was only observed at low temperatures in the condensed phase.[12] This symmetrical dioxide was detected in 1990 in the gas phase in the reaction of Br_2 with atomic oxygen[13] and identified as a paramagnetic molecule with C_{2v} symmetry. The visible spectrum of gaseous OBrO has been reported only in 1994,[14] and spectroscopic evidence of its formation as an intermediate in the BrO + O_3 reaction was presented very recently.[15]

The experimental information about the unsymmetrical BrOO isomer is much more fragmentary. The harmonic vibrational frequency for the OO stretch was reported in 1978,[16] but no experimental measurements exist for the other vibrational frequencies. This dioxide is thought to be kinetically unstable, decomposing instantly into Br + O_2 with an estimated Br−OO bond energy of about 1 kcal/mol.[17] BrOO has been proposed as an intermediate in the parallel channel of a branching process associated with the mentioned reaction of BrO with O_3.[15] The other mechanism currently considered as a major path for bromine-controlled ozone loss has been associated with the self-reaction of BrO[5] which is suggested to go through a Br_2O_2 intermediate. This molecule can be deactivated by collision leading mostly to Br_2 and O_2 or can decompose to Br and BrOO.

In light of these considerations, the *ab initio* study of bromine dioxides, especially the unsymmetrical BrOO isomer, may help to elucidate certain molecular characteristics of atmospheric processes involving bromine. Moreover, it must be stressed that most of the speculations on the role of BrOO in such processes happen to be based on the mentioned 1 kcal/mol estimate for the energy of the bond between bromine and the OO fragment of this radical. This energy was obtained by Blake et al. in 1970[17] in the course of a study of recombination rate constants of bromine atoms with different inert third bodies including the oxygen molecule, and it was determined by assuming Lennard-Jones interaction potentials and other improved model potentials. For the particular Br−O_2 interaction, potential depths in the range 0.76−2.52 kcal/mol were obtained, which after the proper refinement analysis led to a most probable depth of 0.95 kcal/mol.[17] Unfortunately the method employed by Blake et al. was not suitable for determining the potential depth position except when bromine interacts with rare gas atoms, and thus, no Br−O_2 equilibrium distance has ever been proposed for this interaction.

We present in this work an *ab initio* study of bromine dioxides, focusing especially on BrOO. Valence-only correlated calculations to various levels of the theory using effective core potentials have been carried out. Since sufficiently flexible basis sets are needed to achieve reliable results, we have developed

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bases of triple-ζ quality plus two sets of d and one set of f polarization functions, especially suited to the effective core potential model used, namely, the averaged relativistic effective potential (AREP) approach.[18,19] The development of these basis sets as well as a brief overview of the computational methodology employed is presented in the following section. Results obtained at different levels of the theory are next reported and discussed in connection with theoretical and experimental information existing for the analogous OClO/ClOO system. The main conclusions are finally presented.

Computational Methods

Equilibrium geometries have been determined at UMP2 and CCSD(T) levels of the theory in valence-only calculations using *shape-consistent* effective core potentials (ECP)[18] in all the atoms. The same electron valence spaces are retained for halogens so that the computational effort required to treat chlorine and bromine dioxides is completely equivalent. The particular ECP formulation employed, the AREP procedure,[19] implicitly accounts for relativistic effects in heavy atoms in standard nonrelativistic theoretical treatments. However, relativistic corrections for compounds having third-row main elements like bromine are expected to be small enough to not be a problem in determining molecular parameters in *ab initio* calculations.[20] For example, accurate calculations for one molecule with another third-row element (SeH_2) have shown that relativistic corrections are responsible for a shortening of 0.003 Å in bond lengths, virtually no effect on bond angles, and lowerings less than 10 cm^{-1} in harmonic frequencies.[21]

UMP2 calculations on doublet radicals like the halogen dioxides which constitute the object of this work may suffer from spin contamination from higher spin states. Although initial UHF expectation values of the S^2 operator are a direct measure of the degree of spin contamination at a given structure, the changes of $\langle S^2 \rangle$ will provide a more valuable tool to explore spin contamination effects when computing gradients or vibrational frequencies. Jensen[22] has demonstrated that the errors in vibrational frequencies arising from spin contamination are related to the geometrical derivative of $\langle S^2 \rangle$ rather than to $\langle S^2 \rangle$ itself. This problem is investigated in our UMP2 calculations by discussing expectation values of S^2 as well as their derivatives, especially when considering vibrational frequencies and paths along potential energy surfaces far from the minima. All the calculations were performed with GAUSSIAN94.[23]

The valence-only basis sets used in this work are an implementation for AREP operators of the correlated consistent cc-pVTZ sets by Dunning[24] which are [3s3p2d1f] contractions of (5s5p2d1f) primitive sets. Since general cc-pVXZ-type sets (X = D for double, T for triple, Q for quadruple, 5 for quintuple) were not available for general ECP calculations, we have adapted the (sp) valence segments of Dunning's sets for oxygen and chlorine by reoptimizing the exponents in HF valence-only atomic calculations using AREPs. Polarization d and f exponents given by Dunning have been kept unchanged after checking that reoptimizing them led to negligible energy lowerings in correlated atomic calculations at the same level used by Dunning (CISD). Because these basis sets were not developed for third-row atoms, we have constructed new complete valence-only sets for bromine following a similar scheme to that prescribed by Dunning.[24] In order to find optimum compromises between flexibility and ease of computation, we started developing DZ, TZ, and QZ valence-only bases. We then investigated the performance of these basis sets in the treatment of correlation effects, following systematic atomic analyses like those carried out to construct original cc-pVXZ sets. After preliminary calculations on benchmark atomic and molecular systems with exploration of basis set superposition errors, we selected a valence-only triple-ζ set with polarization functions identical to those of cc-pVTZ. The final TZ basis sets chosen represent an acceptable compromise between flexibility and affordable computer times in molecular calculations. Gaussian exponents and contraction coefficients of these (5s5p2d1f)/[3s3p2d1f] basis sets, hereafter denoted AREP/TZ(2df), are given in Table 1 for the atoms considered in this work.

TABLE 1: AREP/TZ(2df) Gaussian Exponents (α) and Contraction Coefficients (*c*) for Oxygen, Chlorine, and Bromine Atoms

	oxygen		chlorine		bromine	
	α	*c*	α	*c*	α	*c*
(s)	89.77	−0.017 691	10.01	−0.064 606	10.07	−0.003 543
	14.95	−0.211 398	4.465	0.472 723	3.953	0.197 379
	5.675	−0.808 043	2.722	−1.398 527	1.917	−1.173 846
	0.9853	1.0	0.4788	1.0	0.4416	1.0
	0.2996	1.0	0.1749	1.0	0.1530	1.0
(p)	35.27	0.040 294	13.38	−0.041 377	7.601	−0.165 411
	7.889	0.255 280	2.451	−0.194 335	3.444	1.198 346
	2.307	0.805 373	0.9206	1.140 892	2.726	−2.048 473
	0.7207	1.0	0.3628	1.0	0.4700	1.0
	0.2154	1.0	0.1283	1.0	0.1451	1.0
(d)	2.314	1.0	1.046	1.0	0.439	1.0
	0.645	1.0	0.344	1.0	0.146	1.0
(f)	1.428	1.0	0.706	1.0	0.401	1.0

TABLE 2: *Ab Initio* Theoretical and Experimental Molecular Constants for the Ground States of Diatomic Oxides ^{35}ClO and ^{79}BrO[a]

	r_e	ω_e	$\omega_e x_e$	B_e	$\alpha_e \times 10^3$	$D_e \times 10^7$
			ClO			
UMP2[b]	1.567	848.3	7.9	0.6256	4.9	13.6
CCSD[b]	1.586	845.9	5.0	0.6106	5.8	12.7
CCSD(T)[b]	1.592	832.7	5.3	0.6061	5.9	12.8
QCISD[c]	1.578	854.3	4.9	0.6171	5.6	12.9
QCISD(T)[c]	1.580	840.9	6.7	0.6153	6.4	13.2
exptl	1.5696[d]	853.72[e]	5.58[e]	0.6235[e]	5.94[e]	13.3[e]
			BrO			
UMP2[b]	1.721	747.4	10.2	0.4335	0.4	5.8
CCSD[b]	1.727	726.6	3.3	0.4249	3.4	5.8
CCSD(T)[b]	1.732	717.4	4.2	0.4225	3.6	5.9
QCISD[c]	1.729	728.0	2.6	0.4242	3.2	5.8
QCISD(T)[c]	1.731	705.8	6.5	0.4232	4.1	6.1
exptl	1.7207[f]	725.69[f]	4.74[f]	0.4281[f]	3.64[f]	5.94[f]

[a] Bond distances (r_e) are in Å; harmonic vibrational frequencies (ω_e) and anharmonic vibrational ($\omega_e x_e$), rotational (B_e), vibration−rotation coupling (α_e), and centrifugal distortion (D_e) constants are in cm^{-1}. [b] AREP/TZ(2df) calculations, this work. [c] AE/6-311+G(3df) calculations from ref 25. [d] Reference 26. [e] Reference 27. [f] Reference 28.

As a first illustration on the performance of AREP/TZ(2df) basis sets, we present in Table 2 some molecular constants for diatomic monoxides ClO and BrO. Our theoretical UMP2, CCSD, and CCSD(T) results are compared with experimental measurements and very recent *ab initio* QCISD and QCISD(T) all-electron (AE) calculations by McGrath and Rowland[25] using 6-311+G(3df) basis sets. Spectroscopic parameters have been determined from Dunham analyses of potential energy curves fitted to nine points per curve in the region $r_e \pm 0.125$ Å. As is evident from this table, UMP2/AREP/TZ(2df) calculations provide fairly good bond distances in both oxides and acceptable estimates of spectroscopic parameters, although the anharmonicity exhibits larger errors in both radicals, especially in BrO. Except for geometries, coupled cluster curves provide overall better molecular constants. The inclusion of the triples contribution to both CCSD/AREP and QCISD/AE methods gives place to the same behavior: larger bond lengths, lower harmonic frequencies, larger anharmonicities and essentially unaltered

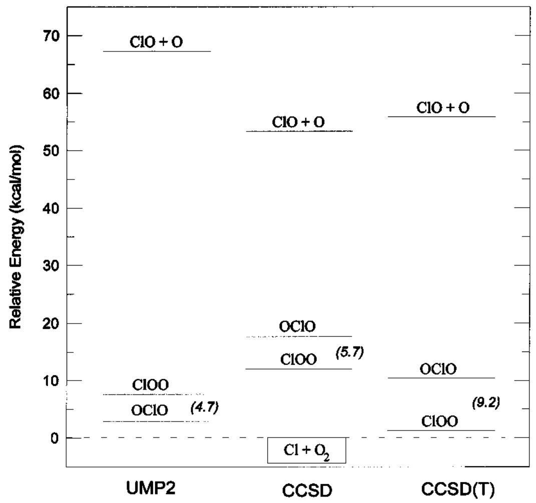

Figure 1. Energies of electronic ground states of OClO and ClOO isomers and energy for dissociation into ClO + O relative to the dissociated system Cl + O_2 obtained in *ab initio* valence-only AREP/TZ(2df) calculations at the UMP2, CCSD, and CCSD(T) levels of the theory at UMP2 geometries. Energy differences (kcal/mol) between OClO and ClOO are indicated in parentheses.

values for the other constants. It is worth remarking on the general good performance of the AREP/TZ(2df) treatment, especially highlighted by the fact of being compared with experimental data and the most accurate available *ab initio* results obtained with larger basis sets.

Results and Discussion

Although our attention is focused on OBrO and BrOO, we discuss also some results for chlorine dioxides. Since both theoretical and experimental reference data exist for OClO and ClOO, these results may help to calibrate the reliability of some predictions regarding particular properties on bromine dioxides. Moreover, many considerations regarding doublet radicals like these XO_2 species are common to both halogen systems. The reader is refered to the fundamental papers by Vaida and Simon[8] on the experimental side and Peterson and Werner[10] on the theoretical one for valuable information concerning chlorine dioxides.

Relative energies computed with AREP/TZ(2df) basis sets at the UMP2, CCSD and CCSD(T) levels of the theory at UMP2 geometries for OClO/ClOO and OBrO/BrOO systems are presented in Figures 1 and 2, respectively. Although CCSD(T) geometries have been determined for bromine dioxides, we have not tried to optimize structures at this level for OClO/ClOO. The difference between CCSD(T) energies computed at UMP2 geometries and CCSD(T) energies corresponding to geometrical structures optimized with this method amounts to 0.09 kcal/mol for OBrO and 0.77 kcal/mol for BrOO. If one reasonably assumes the same magnitude for differences in CCSD(T) energies in OClO/ClOO, the changes in the position of OXO symmetrical dioxides in these figures are negligible, but XOO isomers should be about 0.8 kcal/mol below, increasing the CCSD(T) gap between them to 10.0 kcal/mol for chorine dioxide and 12.5 kcal/mol for bromine dioxide.

As stated in the Introduction, the unsymmetrical ClOO isomer is thermodynamically more stable, although it quickly dissociates releasing atomic chlorine. The correct energetic ordering of ClOO and OClO in our calculations is only obtained when the electron correlation is treated by means of coupled cluster methods. At the three levels of theory considered, the minimum energy corresponds to the dissociation products Cl + O_2, whereas the other possible channel for dissociation into ClO + O is much higher in energy. From measured dissociation energies for both channels, the experimental difference between Cl + O_2 and ClO + O may be set in 56 ± 2 kcal/mol.[10] Contracted multireference CI (CMRCI) AE calculations by Peterson and Werner employing a cc-pVQZ basis set for oxygen and a (17s12p3d2f)/[6s5p3d2f] set for chlorine place the ground state of ClOO 12.7 kcal/mol below OClO and predict for the difference between Cl + O_2 and ClO + O an energy of 58 kcal/mol. Our higher-level CCSD(T) results are 10 and 56 kcal/mol for both energies, which compare well with these CMRCI reference theoretical values. However, considering the nature of all these correlated calculations, our slightly better result for the OClO/ClOO energy when compared with the experimental estimate must be regarded as fortuitous. It must be remarked that CASSCF calculations performed by Peterson and Werner yield rather poor results in describing these energetic separations, which indicates very large dynamical electron correlation effects in these dioxides.[10] Relative energies for bromine dioxides OBrO and BrOO in Figure 2 exhibit exactly the same pattern as in Figure 1, which allows one to assume that bromine dioxides present the same energetic ordering of isomers as in the OClO/ClOO system. Taking for reference our coupled cluster results and experimental data and assuming in the bromine system the same type of errors as in chlorine dioxides (CCSD(T)/AREP 10 kcal/mol versus experimental 4 kcal/mol), it may be predicted that BrOO has to lie energetically below OBrO by about 5 kcal/mol. For both bromine isomers it is also obvious that the preferred dissociation channel goes to Br + O_2 and that the dissociation into BrO + O requires more than 50 kcal/mol.

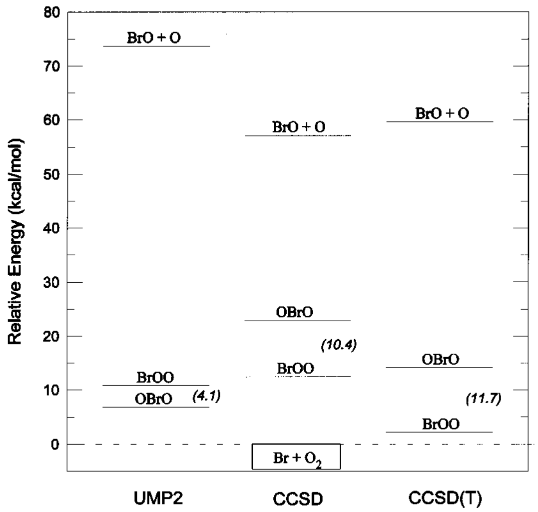

Figure 2. Energies of electronic ground states of OBrO and BrOO isomers and energy for dissociation into BrO + O relative to the dissociated system Br + O_2 obtained in *ab initio* valence-only AREP/TZ(2df) calculations at the UMP2, CCSD, and CCSD(T) levels of the theory at UMP2 geometries. Energy differences (kcal/mol) between OBrO and BrOO are indicated in parentheses.

For molecules of higher spin multiplicity like XO_2 doublet radicals, UMP2 calculations are known to suffer from contamination of unwanted spin states that may lead eventually to distortions of the potential energy surface. Spin contamination can be removed by means of projection operators[29] obtaining projected MP2 (PMP2) energies, noticeably lower than UMP2 energies even when annihilating only the contamination from the next-higher spin state. For the doublet ($s(s + 1) = 0.75$) systems studied, initial UHF $\langle S^2 \rangle$ values found in optimized UMP2 structures were 0.783 for OClO, 0.769 for ClOO, 0.789 for OBrO, and 0.769 for BrOO, which indicate no significant spin contamination. After annihilating the first spin contami-

TABLE 3: Geometries, Dipole Moments, and Harmonic Frequencies for theGround States of Chlorine Dioxides OClO and ClOO[a]

	UMP2[b]	MP2[c]	CMRCI[d]	exptl	
			OClO		
r_{OCl}	1.485	1.486	1.480		1.470[e]
θ_{OClO}	117.9	118.5	117.8		117.4[e]
μ	1.95	1.99	1.85		1.79[f]
ω_1 sym str	1009	999	945	945.6[g]	944.8[h]
ω_2 bend	444	459	452	447.7[g]	448.7[h]
ω_3 asym str	1187	1136	1095	1110.1[g]	1107.6[h]
			ClOO		
r_{ClO}	2.126	2.181	2.139		1.83[i]
r_{OO}	1.159	1.174	1.201		1.23[i]
θ_{ClOO}	117.6	118.6	115.7		110[i]
μ	1.89		1.11		
ω_1 ClO str	226	194	181	214.9[j]	192.4[k]
ω_2 bend	485	467	391	432.4[j]	408.3[k]
ω_3 OO str	1878	1836	1506	1477.8[j]	1442.8[k]

[a] Bond distances (r) are in Å, bond angles (θ) in deg, dipole moments (μ) in D, and harmonic vibrational frequencies (ω) in cm^{-1}. [b] Valence-only AREP/TZ(2df) calculations, this work. [c] OClO: RMP2/6-311G(2df) AE calculations, ref 30. ClOO: AUMP2/6-31G* AE calculations, ref 22. [d] AE contracted multireference CI calculations (see text for the basis set used), ref 10. [e] Reference 31. [f] Reference 32. [g] Reference 33. [h] Reference 34. [i] Assumed structure in the analysis of the IR matrix spectrum in ref 35. [j] Ar matrix FTIR spectrum, ref 34. [k] Ar matrix IR spectrum, ref 36.

nant, $\langle S^2\rangle$ is 0.758 for OClO, 0.756 for ClOO, 0.761 for OBrO, and 0.757 for BrOO. If the MP2 energetic separation in Figures 1 and 2 is computed with PMP2 energies, the difference increases to 5.5 kcal/mol for OClO/ClOO and 5.0 kcal/mol for OBrO/BrOO. The geometrical derivative of $\langle S^2\rangle$ for analyzing spin contamination in UMP2 vibrational frequencies and geometries far from equilibrium in the potential surface is discussed below.

We compare in Table 3 our UMP2/AREP/TZ(2df) results for chlorine dioxides OClO and ClOO with related MP2 reference values, CMRCI calculations of Peterson and Werner,[10] and experimental data. Considering the nature of the theoretical treatment reported by Peterson and Werner (extensive contracted multireference configuration interaction with very large basis sets), their results must be regarded as the most accurate available data for these radicals. Since one of the objectives of this work, exploring the nature of the bonding in BrOO, demands a good deal of geometry optimizations, we have performed our *ab initio* study at the computationally not too demanding UMP2 level of the theory for exploring geometries and frequencies. Therefore, comparisons in Table 3 are mainly intended to set reasonable margins of reliability for our further results concerning bromine dioxides, where neither experimental nor theoretical complete data are available for reference. For OClO, the UMP2/AREP bond length is only 0.005 Å larger than the CMRCI value, the bond angle is essentially the same, and the dipole moment is 0.1 D larger. As pointed out by Jensen,[22] the error associated with spin contamination in vibrational frequencies depends mainly on the magnitude of $\mathrm{d}\langle S^2\rangle/\mathrm{d}x$: large values of this derivative indicate that the potential curve rises with the coordinate x as more high-energy states are mixed, which leads to higher frequencies. UMP2/AREP/TZ(2df) harmonic vibrational frequencies for bond stretchings are 60−80 cm^{-1} too high, whereas the bending frequency compares well with reference results. As far as the magnitude of errors arising from significant spin contamination is known to be much more larger (hundreds of or even 1000 cm^{-1}!),[22] these results are not indicative of serious spin contamination problems. In fact, the geometrical derivative of $\langle S^2\rangle$ presents values of about 0.014. It must be also stressed that UMP2/AREP frequencies for all the molecules studied in this work are obtained by double numerical differentiation of the energy with step size = 0.005 Å, which is half of the commonly used step sizes for computing harmonic frequencies. We have included in Table 3 restricted MP2 AE results of Rauk et al.[30] obtained with 6-311G(2df) basis sets of similar quality to those of our AREP bases. Considering the distinct treatment of spin in these MP2 calculations, UMP2/AREP and RMP2/AE results show a reasonable agreement.

The ClOO isomer is much more difficult to treat. Even for the electronic ground state, its experimental characterization is far from complete, and only a tentative assumed structure exists from the analysis of IR matrix experiments by Arkell and Schwager,[35] although this experimental study is somewhat outdated. More recently, Müller and Willner[34] and Johnsson et al.[36] have reinvestigated the spectroscopic properties of ClOO under improved experimental conditions. In light of these new measurements, it seems that the *ab initio* structure of Peterson and Werner is more reliable[34,36] especially for the ClO bond length. Our UMP2/AREP/TZ(2df) results are compared with these CMRCI theoretical reference values and with AUMP2/6-31G* calculations by Jensen.[22] This last method is the MP2 implementation of a procedure proposed by Baker[37] in which the contamination from the next-higher spin state is annihilated in each iteration of the SCF procedure, yielding thus an annihilated self-consistent wave function. Since these AUMP2 results are free from the main contribution to spin contamination, the comparison with our UMP2 calculations should provide direct information on the magnitude of this effect for ClOO. Unfortunately, however, the basis set employed by Jensen (6-31G*) is not flexible enough so that AUMP2 results may suffer from slight basis set deficiencies. Notice that the UMP2/AREP ClO bond distance and bond angle compare well with CMRCI values, slightly better than AUMP2 results, though the OO bond length is clearly too short in both MP2 calculations (for O_2 the experimental bond length is 1.208 Å, while the optimized UMP2/AREP/TZ(2df) result is 1.227 Å). Nevertheless, the AUMP2 geometry also shows a OO bond distance that is too short, suggesting that instead of an effect produced by spin contamination problems, this shortening could be a consequence of large charge transfer predicted by MP2 calculations (see below). In fact, the geometrical derivative of $\langle S^2\rangle$ for our UMP2 geometry optimization displays values about 0.025 that, though larger than those of OClO isomer, are not indicative of important spin contamination. It may be worth remarking that although the study of these and other difficult halogen peroxide systems should require higher levels of the theory for reaching close agreement with experiment, a good deal of information can be obtained from lower-level treatments like UMP2 calculations, provided that basis sets of appropriate quality are used. For illustrative examples on the ClOOCl molecule, the reader is referred to the set of results in Tables 1 and 2 of ref 38 and to ref 39 for other isomers of Cl_2O_2.

Comparing their OO bond length with that calculated for O_2 with the same methodology, Peterson and Werner conclude that the slightly shorter distance in ClOO is indicative of charge transfer from O_2 to Cl resulting in a polarity $^{-}\mathrm{Cl}-\mathrm{O_2}^{+}$, which is confirmed by the sign of their computed dipole moment. In addition, the small Cl−OO binding CMRCI energy along with the associated large ClO bond distance lead to a stretching frequency that is too small ($\omega_1 = 181$ cm^{-1}). Although the authors argue that the measured stretching frequency in IR matrix experiments should be larger than the actual gas phase value, the small ω_1 theoretical value seems to be the conse-

TABLE 4: AREP/TZ(2df) Geometries for the Ground States of Bromine Dioxides OBrO and BrOO[a]

	UMP2	CCSD(T)
	OBrO	
r_{OBr}	1.640	1.650
θ_{OBrO}	115.4	114.9
	BrOO	
r_{BrO}	2.258	2.291
r_{OO}	1.168	1.214
θ_{BrOO}	118.3	116.4

[a] Bond distances (r) are in Å, bond angles (θ) in deg.

quence of a too weak bond. The ω_3 frequency is essentially the OO stretching, and due to the high sensitivity of this bond to the amount of charge transfer, the larger vibrational frequency seems now to be the byproduct of a bond strengthened by that transfer. UMP2/AREP/TZ(2df) results for ClOO in Table 3 may be understood with the aid of these charge transfer considerations. The anomalously short OO bond distance as well as the too high ω_3 frequency might be indicative of an O_2^+ molecular segment associated with a marked charge transfer. This conclusion is supported by the large dipole moment obtained with the UMP2 electron density (1.89 D as compared with 1.11 D in CMRCI calculations) as well as by the population analyses carried out (see below). The polarity is essentially associated with the ClO bond, and the dipole moment orientation happens to lie nearly along this bond. Note again that, in spite of the removal of spin contamination in his AUMP2 calculations, Jensen[22] obtained also a too high frequency for OO stretching, 1846 cm^{-1}, much closer to our value than to experimental or CMRCI data. The lower ω_1 AUMP2 frequency for ClO stretching seems a consequence of the large ClO bond length predicted by this method, 2.181 Å instead of 2.126 Å given by UMP2/AREP.

We present in Table 4 geometries optimized in UMP2 and CCSD(T) valence-only calculations using AREP/TZ(2df) basis sets for bromine dioxides OBrO and BrOO. Initial UHF $\langle S^2\rangle$ values are 0.789 for OBrO and 0.769 for BrOO, being the corresponding geometrical derivatives of this expectation value in the vicinity of equilibrium structures about 0.015 and 0.010, respectively, which demonstrates that no significant spin contamination effects are present in finding optimized geometries. The close agreement between UMP2 and CCSD(T) geometries for the symmetrical oxide allows predicting for bond length and bond angle values of about 1.65 Å and 115°, respectively. The UMP2 geometry of BrOO presents the same features as ClOO when comparing with higher-level results, CMRCI for chlorine oxides or CCSD(T)/AREP for bromine oxides. The BrO bond length is only 0.03 Å shorter and the bond angle about 2° larger, while the OO bond is again too short. On the basis of results in Table 4, for BrOO we tentatively predict bond distances of 2.28 and 1.21 Å for BrO and OO, respectively, and a bond angle of about 116°, essentially the same geometry as for ClOO except for the obviously larger halogen−oxygen bond. The short UMP2 value for OO bond length seems again associated to a strong charge transfer. If we represent XOO isomers as $XO_{(1)}O_{(2)}$, Mulliken atomic charges computed with the UMP2 density for BrOO are −0.155 for Br, +0.151 for $O_{(1)}$, and +0.004 for $O_{(2)}$, while for chlorine dioxide they are −0.187 for Cl, +0.165 for $O_{(1)}$, and +0.022 for $O_{(2)}$. A separate natural bond orbital (NBO) analysis[40] yields −0.118 for Br, +0.138 for $O_{(1)}$, and −0.020 for $O_{(2)}$ in bromine dioxide BrOO and −0.170 for Cl, +0.169 for $O_{(1)}$, and +0.001 for $O_{(2)}$ in the ClOO case. The qualitative picture of UMP2 charge transfer is essentially identical in BrOO and ClOO, the polarity being associated almost entirely with the XO bond in accordance with the MP2 dipole moment orientation which lies nearly along this bond in both halogen radicals. Values of the dipole moment computed with UMP2/AREP/TZ(2df) valence-only calculations at UMP2/AREP geometries are given in Table 5 for OBrO and BrOO. The slightly lower amount of charge transfer found in BrOO and the larger Br−$O_{(1)}$ distance as compared to that of Cl−$O_{(1)}$ in ClOO yield for the dipole moment of BrOO 1.41 D, clearly smaller than μ(ClOO). If deviations with respect to higher-level reference data in Table 3 are taken as ground for extrapolating trends, the true dipole moment for BrOO should be likely about 0.75 D, whereas for OBrO a magnitude of about 2.5 D might be suggested.

TABLE 5: UMP2/AREP/TZ(2df) Dipole Moments μ (D) and Harmonic Frequencies ω (cm^{-1}) for the Ground States of Bromine Dioxides OBrO and BrOO

OBrO		BrOO	
μ	2.61	μ	1.41
ω_1 sym str	897	ω_1 BrO str	156
ω_2 bend	328	ω_2 bend	439
ω_3 asym str	939	ω_3 OO str	1581

Harmonic vibrational frequencies in Table 5 are also in agreement with the behavior exhibited by frequencies in chlorine oxides in Table 3. The larger OBr distance in OBrO as compared with the OCl bond in OClO and the smaller bond angle in UMP2 results lead to slightly lower frequencies in the three vibrational modes for this symmetrical bromine dioxide. Assuming similar relative errors as for OClO (7% for both stretching modes and 1% for bending), vibrational harmonic frequencies about 830 and 875 cm^{-1} for symmetrical and asymmetrical stretching, respectively, and 325 cm^{-1} for bending may be tentatively predicted for OBrO. Vibrational frequencies for BrOO in Table 5 reveal the expected features when comparing with ClOO if one now considers the weaker nature of bonds in BrOO. For the fundamental OO stretching mode, there exists an experimental value, $\omega_3 = 1487$ cm^{-1}, measured years ago,[16] which is similar to the corresponding frequency measured for ClOO, 1443−1478 cm^{-1}. The OO stretching frequency first obtained with standard numerical procedure and step size = 0.005 Å in BrOO was 1776 cm^{-1}, too high a value for bringing up a simple calibration to get a meaningful value for this vibrational mode. In order to obtain a more reliable estimate of this frequency, we have calculated a UMP2/AREP/TZ(2df) potential energy curve for the OO stretching by optimizing the whole geometry at eight OO distances in an interval of 0.16 Å around the equilibrium value (1.168 Å). With the improved force constant for the OO stretching, the whole **F** matrix is constructed so that the set of frequencies displayed in Table 5 are determined with the usual **FG** matrix analysis. The change in this frequency after optimizing the procedure for calculating ω_3 is dramatic: the new value is almost 200 cm^{-1} lower (the shallowness of the potential energy surface for this molecule as described below may be the reason for the initial poor frequency). It is worth remarking that final harmonic frequencies for bending and BrO stretching change less than 8 cm^{-1} with respect to former values, which is the expected result if one takes into account the rather different magnitudes of these frequencies and ω_3.

We finally discuss the nature of bonding in BrOO by exploring selected scans of the potential energy surface. After some preliminary numerical work, it is found that the more stable path in this surface corresponds to θ_e(BrOO) = 118° (UMP2/AREP minimum), whereas variations in bond angles in the proximity of this value rapidly lead to more unstable geometrical arrangements but still present bound states. We

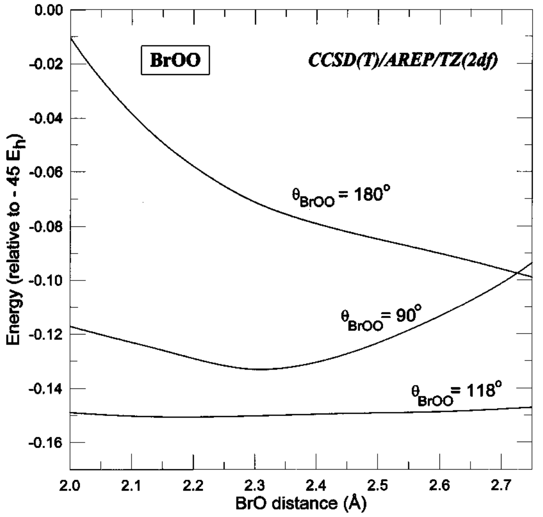

Figure 3. One-dimensional sections of the computed energy surface of BrOO obtained in *ab initio* valence-only AREP/TZ(2df) calculations for three angular arrangements: equilibrium UMP2 bond angle (118°), bromine atom perpendicular to OO axis, and linear geometry. The energy is computed at the CCSD(T) level as a function of the BrO bond length with UMP2 optimized OO bond distances.

display in Figure 3 one-dimensional cuts of the potential energy surface for three bond angles, 90°, 118°, and 180°. The range of BrO bond distances goes from 2.0 to 2.75 Å, a maximum value at which geometries can be optimized without encountering discontinuities and problems due to deep spin contamination problems. For every θ, the OO bond distance is optimized in UMP2/AREP calculations for seven BrO bond distances and then the CCSD(T) energy is calculated at these UMP2 geometries. While in the vicinity of equilibrium structure (around $r_{\mathrm{BrO}} = 2.3$ Å), initial UHF $\langle S^2 \rangle$ values are about 0.770 and the derivative d $\langle S^2 \rangle / \mathrm{d}r_{\mathrm{BrO}}$ is about 0.010; for BrO bond lengths in the 2.60−2.70 Å region, $\langle S^2 \rangle$ increases to 0.825 and the derivative raises too steeply: we have cut the scan of the potential energy surface at BrO bond lengths for which spin contamination as given by the $\mathrm{d}\langle S^2 \rangle / \mathrm{d}r_{\mathrm{BrO}}$ criterion is unacceptably high.

As is apparent from Figure 3, the potential curve for the 90° angle is much less flat than of the 118° equilibrium angle and presents a minimum ~11 kcal/mol above the ground state. The expectation value of UHF S^2 is now about 0.830 and its geometrical derivative about 0.015 in the region of the minimum, but spin contamination increases rapidly as the bromine atom is moved outwards; thus for $r_{\mathrm{BrO}} = 2.6$ Å, the derivative has increased to 0.39, although $\langle S^2 \rangle$ is about 0.795. The potential curve for linear BrOO is repulsive, with fast energy increases as BrO distance decreases in the region displayed. Spin contamination is now less marked than for $\theta_{\mathrm{BrOO}} = 90°$, with changes in the derivative of $\langle S^2 \rangle$ of about 0.04 except for innermost points where it raises to 0.2. For practically the whole 180° curve $\langle S^2 \rangle$ is about 0.780. Changes in the optimized UMP2/AREP OO bond distances found in these calculations exhibit distinct features for the three one-dimensional cuts of the energy surface analyzed. For the ground state, the OO bond distance presents a minimum (1.168 Å) and increases rapidly with smaller BrO distances and much more slowly as Br separates from oxygen atoms. For bromine perpendicular to $O_{(1)}$, the $O_{(1)}O_{(2)}$ bond length diminishes continuously from 1.212 Å at $r_{\mathrm{BrO}} = 2.0$ Å until 1.160 Å at $r_{\mathrm{BrO}} = 2.75$ Å, with an equilibrium value of 1.176 Å. Finally, for the repulsive curve of linear BrOO, interoxygen distance increases continously as energy raises, going in the interval displayed in Figure 3 from 1.260 Å at $r_{\mathrm{BrO}} = 2.75$ Å to 1.323 Å at $r_{\mathrm{BrO}} = 2.0$ Å.

As expected from the results presented before, the energy curve for the equilibrium bond angle is extremely flat: from the minimum at $r_{\mathrm{BrO}} = 2.26$ Å until a BrO separation of 2.75 Å, the energy increases by only 1.2 kcal/mol (1.9mE_h). Since the dissociation limit Br + O_2 given by CCSD(T) calculations is 2.25 kcal/mol (see Figure 2) below the ground state of BrOO, these results indicate that only a small barrier exists for that dissociation. Although with the methodology employed it is not possible to determine the precise form of this barrier, our calculations suggest that bromine is bound to oxygens by *at least* 1.2 kcal/mol. On the other side, Mulliken atomic charges from UMP2 density at $r_{\mathrm{BrO}} = 2.75$ Å are −0.056 for Br and +0.040 and +0.015 for $O_{(1)}$ and $O_{(2)}$, respectively, which reveals that the amount of charge transfer when going from $r_{\mathrm{BrO}} = 2.26$ to 2.75 Å is drastically decreased, as expected. Considering this low charge transfer and the shallowness of the energy curve, it should be unreasonable to expect an energy increase larger than 0.5 kcal/mol from the outer BrO bond length limit in Figure 3 to the top of the barrier. The characterization of the bonding in the BrOO radical given by these results allows us to tentatively suggest for BrOO dissociating into Br + O_2 an energy barrier between 1.2 and 1.7 kcal/mol, which is in good agreement with the only experimental estimate existing since 1970.[17]

Conclusions

Basis sets of triple-ζ quality plus two sets of d and one set of f polarization functions have been optimized for use with averaged relativistic effective potentials (AREP) in *ab initio* valence-only calculations for chlorine and bromine dioxides. The good performance of these AREP/TZ(2df) sets is firstly illustrated by computing spectroscopical constants for ground states of ClO and BrO in UMP2, CCSD, and CCSD(T) calculations. These results are in close agreement with reference experimental data and highly accurate *ab initio* calculations.[25−28]

Optimized geometries for bromine dioxides OBrO and BrOO are determined in UMP2 and CCSD(T) valence-only AREP/TZ(2df) calculations. Dipole moments and harmonic vibrational frequencies at UMP2 geometries are obtained at the UMP2/AREP/TZ(2df) level, while energies at these geometries are computed using the CCSD and CCSD(T) procedures. Spin contamination effects in UMP2 results are discussed by analyzing UHF $\langle S^2 \rangle$ expectation values as well as their derivatives[22] in the determination of vibrational frequencies and potential energy surface scans. The BrOO isomer is found to be energetically more stable than the symmetrical OBrO dioxide in 5 kcal/mol. Both dioxides dissociate into Br + O_2, this path being more than 50 kcal/mol lower than the dissociation into BrO + O. The overall energetic description agrees with results here obtained for the OClO/ClOO system for which both high-level *ab initio* calculations and experimental measurements exist.[10]

The bonding in BrOO is studied at the CCSD(T)/AREP/TZ(2df) level, analyzing one-dimensional cuts of the energy surface for three bond angles, 118° (UMP2 minimum), 90°, and 180°. The ground state energy surface is extremely flat, while the linear geometry for BrOO leads to repulsive energy curves for the whole range of Br−OO distances considered. Similar to the analogous chlorine dioxide, computational evidence of marked charge transfer from OO to Br is found, the polarity in this molecule being almost entirely associated with the Br−O bond. Since the dissociated system is ~2 kcal/mol lower in energy, only a small barrier is likely to exist for BrOO dissociating into Br + O_2. Within the limits imposed by the methodology employed and the energy surface region explored, we suggest a barrier height between 1.2 and 1.7 kcal/mol for breaking the bond between bromine and oxygen atoms. This result is in reasonable agreement with the only experimental measurement existing for the bonding in this radical since 1970, where a van der Waals-like interaction between Br and O_2 was assumed.[17]

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Note Added in Proof. Upon completion of the manuscript, Müller et al.[41] have published the submillimeter spectrum and the IR spectrum in the region of the ν_3 fundamental of the bromine dioxide OBrO radical in the gas phase. The geometry obtained from these measurements is the following: $r_{\mathrm{OBr}} = 1.649$ Å and $\theta_{\mathrm{e}} = 114.44°$, which is in excellent agreement with our predicted structural parameters, 1.65 Å and 115°, respectively. These authors measured also the asymmetric stretching frequency $\omega_3 = 851.2$ cm^{-1} and proposed $\omega_1 = 794.6$ cm^{-1} for the symmetric stretching and $\omega_2 = 311$ cm^{-1} for bending, although this last mode was not observed directly. Our UMP2/AREP/TZ(2df) suggested values (875, 830, and 325 cm^{-1}, respectively) have to be compared with these data.

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