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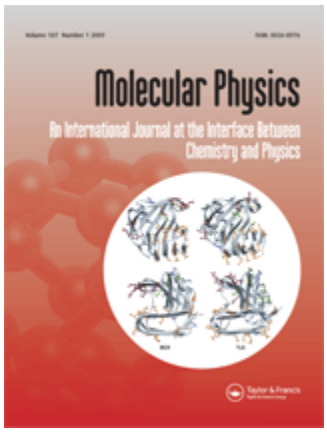

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RESEARCH ARTICLE

Electronically Excited States of XOONO (X = Cl, Br): Theoretical Studies

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Vertical electronic excitation energies of ClOONO and BrOONO, molecules relevant to atmospheric chemistry, were studied using ab initio multireference configuration interaction (MRD-CI) method with the cc-pVDZ and cc-pVTZ basis sets enlarged by s(N) and p(Cl/Br) long-range functions. The dominant transitions in the electronic spectra of ClOONO and BrOONO are calculated at 5.98 eV and 5.19 eV, respectively, with strong intensity and at 5.18 eV and 4.42 eV, respectively, with moderate intensity. Both transitions show multi-reference character, corresponding to linear combinations of the n(O) $\rightarrow \pi^*$ (N-O) type and n(O), σ^*(Cl/Br-O) $\rightarrow \pi^*$(N-O) charge transfer type transitions. Thus, the transitions in the chlorine analogue lie about 0.8 eV higher in energy than in the bromine compound, i. e., the transitions are red-shifted by 32 nm and 42 nm, respectively, from ClOONO upon replacement of chlorine by bromine. The HOMO → LUMO transition can be considered as a n(Cl/Br) $\rightarrow \sigma^*$ (O-Cl/Br) type and is less intense.

Keywords: Electronic spectrum; Halogen peroxynitrite; Multireference configuration interaction calculation

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1. Introduction

The chemistry of halogen (X = Cl, Br) and nitrogen containing compounds is of particular interest to stratospheric ozone depletion studies. Although the bromine compounds are more than 100 times less abundant than the chlorine species, bromine is about 40 times more efficient than chlorine for Antarctic ozone loss [1, 2]. Over the last several decades, there has been considerable work devoted to the characterization of chlorine and bromine source and reservoir species in the atmosphere. In 1976, Rowland et al. [3, 4] first suggested that $ClONO_2$ is a major temporary reservoir for active chlorine. Its later detection in the stratosphere [5] has initiated numerous laboratory studies to elucidate the chemistry of NO_x and ClO_x coupling reactions. The stratospheric significance of $BrONO_2$ was reported by Spencer and Rowland [6] on the basis of UV and IR absorption characteristics measurement and the rate of formation from BrO and NO_2 estimation.

Model simulations and field studies of simultaneous nighttime NO_2 and OClO profile can achive better agreement if the formation of halogen peroxynitrites, ClOONO and BrOONO, as less stable isomers of halogen nitrates, $ClONO_2$ and $BrONO_2$, respectively, were assumed to occur in the cold conditions of the polar stratosphere [7]. On the other hand, the involvment of BrOONO cannot account for the difficulties of fitting the data when master equation models were employed on the combination BrO + NO_2 reaction [8]. Already in 1980 Molina et al. [9] have reported an indication of ClOONO isomers formation in the NO_2 + ClO reaction, but further experiments have provided conflicting conclusions on its formation [10, 11]. Structural information of $ClONO_2$ and $BrONO_2$ have come from gas-phase spectroscopic studies [12]. Several ab initio studies on the structure and vibrational frequencies of $ClONO_2$ and ClOONO have been conducted [13–17]. The recent study on the reaction patway of the ClO + NO_2 reaction has examined the formation of $ClONO_2$ and ClOONO including their isomerization [18]. Theoretical characterization of $BrONO_2$ has been a subject of two papers of Parthiban et al. [19, 20]. Further, the conformational preference of BrOONO [21] and $BrONO_2 \leftrightarrow$ BrOONO isomerization [22] have been reported. To date, no evidence for the existence of the bromine

peroxynitrite isomer was found in IR spectroscopic studies [23, 24].

Understanding the photochemistry of these halogen-containing peroxinitrites is important to the investigation of the overall function of halogen containing species in ozone destruction. As pointed out by Lee et al. [25, 26] the lowest singlet excited states of the penta-coordinated Br species occur at too high an energy for it to be destroyed by solar radiation in the lower stratosphere, while the mono- and tri-coordinated Br species will not be photostable due to the electronic states being accessible to the available radiation from the actinic flux. UV spectrum of monovalent chlorine compound $ClONO_2$ has been probed by Rowland et al. [3] and Manson et al. [27]. The temperature dependence of the UV absorption cross sections has ben determined by Molina et al. [28] and Burkholder et al. [29]. Calculations of excited electronic states of $ClONO_2$ at the CCSD level of theory have been provided by Grana et al. [30], while Mühlhäuser et al. [31] have calculated exited states for the both $ClONO_2$ and $BrONO_2$ with MRD-CI method. Until now there have been no reports in the literature of the electronic absorption spectra of ClOONO and BrOONO, however, the open question is whether they possess the excited electronic states, which make them easily photodissociated in the lower stratosphere.

The aim of the present study is to provide characteristic fingerprints for identifying ClOONO and BrOONO in UV-Vis experiments and to characterize the nature of electronic transitions based on qualitative molecular orbital consideration. We report the results of multireference configuration interaction calculations, MRD-CI, of vertical excitation energies for transitions from ground state to the low-lying singlet and triplet states and corresponding oscillator strengths for dipole-allowed processes. The effect of halogenation on the transition energies of the electronic spectra are discussed.

2. Computational Methods

The geometries of halogen peroxy nitrites were fully optimized using the single and double excitation coupled-cluster method, including a perturbation estimate of the effects of connected triple excitations CCSD(T) [32], with the 6-311G(d) basis set for ClOONO and

cc-pVDZ basis set for BrOONO using the Gaussian 03 program package [33].

The computations of the electronically excited states were performed with the multi-reference single and double excitation configuration interaction method, MRD-CI, implemented in the Diesel program [34]. We used the correlation consistent AO basis sets of Dunning of double and triple zeta quality [35, 36]. In addition both basis sets were enlarged by s-Rydberg functions located at the nitrogen and by a negative ion function for the halogen atom, thus giving the cc-pVDZ+sp and cc-pVTZ+sp basis sets. The exponents taken are $\alpha_s(N) = 0.028$ $\alpha_p(Cl) = 0.049$ and $\alpha_p(Br) = 0.032$, which has been found to be suitable in previous calculations on chlorine and bromine species [31, 37, 38]. The total number of the basis fuctions for ClOONO and BrOONO amounted to 78 (158) and 87 (167), respectively, for the cc-pVDZ+sp (cc-pVTZ+sp) basis sets. Since bromine is a fairly heavy element the scalar relativistic effect could be significant, but the theoretical studies on BrOOBr species [39] have shown that it does not change the order of the excited states in the valence region, and just slightly decreases the vertical excitation energies by about 0.1 - 0.2 eV systematically. For the calculation of excited states, the 24 valence electrons and 14 valence electrons were treated as active for the cc-pVDZ+sp and cc-pVTZ+sp basis sets, respectively, while the remaining electrons were kept in doubly occupied orbitals defined as frozen-core orbitals. The choice of the number of active electrons in the calculations was based on analysis of the molecular orbitals involved in the selected reference configurations.

Particular parameter values used in the calculations are summarized in Table 1. The selection of the reference configurations by a summation threshold was carried out automatically. We used a summation threshold of 0.85, which means that the sum of the squared coefficients of all reference configurations selected for each state (root, R) is above 0.85. The number of reference configurations for ClOONO was around 60 when 14 electrons being active and increased to about 200 when 24 electron were treated as active. For BrOONO, the number of reference configutations amount to 57 and 145, respectively.

From these sets of reference configurations (mains), all single and double excitations in the form of configuration state functions (CSFs) were generated. All configurations of

these sets with an energy contribution $\Delta E(T)$ above a given threshold T were selected, i.e., the contribution of a configuration larger than this value relative to the energy of the reference set is included in the final wavefunction. Selection thresholds of $T = 10^{-7}$ and $T = 10^{-8}$ hartrees were used for double and triple zeta basis sets, respectively, in case of 14 active electrons. The value of $T = 5\times10^{-8}$ was used for 24 active electrons. The effect of the configurations that contribute less than $T = 10^{-7}$ or $T = 10^{-8}$ or $T = 5 \times 10^{-8}$ hartrees is accounted for in the energy computation ($E(MRD-CI)$) by the perturbative λ-extrapolation [40, 41]. The contribution of higher excitations is estimated by applying Langhoff-Davidson correction formula

$$E(MRD-CI+Q) = E(MRD-CI) - (1-c_0^2)[E(ref) - E(MRD-CI)]/c_0^2$$

where c_0^2 is the sum of squared coefficients of the reference species in the total CI wave-function and $E(ref)$ is the energy of the reference configurations.

For ClOONO (BrOONO), the number of CSFs directly included in the energy calculations are as large as 2.9 (2.1) million and 5.4 (4.7) million for the cc-pVDZ+sp and cc-pVTZ+sp basis sets, respectively, selected from a total space of 52 (23) million and 31 (28) million generated configurations (GC/CSFs), respectively.

3. Results and Discussion

3.1. *The ground state of XOONO (X = Cl, Br)*

The ground electronic state for the both species, ClOONO and BrOONO, is a singlet state of C_1 symmetry, ^{1}A, with the cis-perp (cp) configuration of O-NOO dihedral angle with respect to the NOO-X dihedral angle. The CCSD(T)/6-31G(d) optimized structures are presented in Figue 1. Their structures are similar except the O-X bond being somewhat longer for bromine analogue.

The geometrical parameters of neither ClOONO nor BrOONO are available experimentally but the both species have been characterized theoretically. Previous theoretical studies [13, 15, 17, 21] have predicted that there are two stable conformations of XOONO (X = Cl, Br), namely, the cp global minimum structure and the trans-perp (tp) conformer, which is very close in energy to the cp form. The both conformers differ in the O-NOO

dihedral angle being 180^o for the tp form. The energy difference between two ClOONO conformers is 1.7 (1.6) kcal mol^{-1} at G3//B3LYP [17] (G2(MP2) [18]) levels of calculation, while the difference of 1.9 kcal mol^{-1} for BrOONO conformers was predicted at CBS-QB3 level of theory [22]. The energy barriers of 8.7 kcal mol^{-1} (B3LYP/6-311G(d)) and 9.2 kcal mol^{-1} (B3LYP/6-311G(d)) separate the two conformers of chlorine and bromine analogues, respectively. The cp conformers of halogen peroxynitrites, ClOONO and BrOONO, are less stable than the halogen nitrates, $ClONO_2$ and $BrONO_2$, by 25.5 kcal mol^{-1} (G3//B3LYP) and 25.9 kcal mol^{-1} (CBS-QB3), respectively.

3.2. *The excited state of XOONO (X = Cl, Br)*

To provide information about photoabsorption of ClOONO and BrOONO, we claculated the vertical excitation energies for more stable cp form. The spectra arising from the low-lying excited singlet states of both species are summarized in Table 2. The bold numbers in the table are related to the calculations with cc-pVDZ+sp basis set and 24 valence electrons (out of total 30 valence electrons) treated active in the CI calculations, the ground state electron configuration, (core)(1-15)a^2, is henceforth labeled as (12a)^2. More economic computations with 14 active electrons are performed to compare the transition energies obtained with cc-pVDZ+sp and cc-pVTZ+sp basis sets, the results in the table are written in roman and italics numbers, respectively, the ground state is denoted as (7a)^2 configuration. For the former basis set also triplet excitations are calculated, which are forbidden by spin conservation rule. But the experimental photodisociation studies have shown that spin-orbit coupling has non-negligible influence for some chlorine and bromine species like HOCl, NOCl [42] and HOBr [43] so the weak transitions may also be observed. The excited triplet states of ClOONO and BrOONO involve the same valence excitations, the excitation energies of triplet transitions are also listed in Table 2. For ClOONO, the singlet-triplet splitting of the singlet-triplet pairs presented in the table is in the order of 0.3 to 1.0 eV as can be expected for the valence transitions. In the bromine analogue the splitting extends up to 0.6 eV. When the basis set is increased from cc-pVDZ+sp to cc-pVTZ+sp, the computed excitation energies and transition prob-

abilities for the two basis sets are consistent, the computed vertical excitation energies increased less than 0.10 eV. The inclusion of 24 electrons as active in CI calculations decreases the vertical excitation energies by about 0.1 to 0.2 eV except for the very low intensive $9^1A \leftarrow 1^1A$ and low intensive $4^1A \leftarrow 1^1A$ transitions, where the energies for the both species are about 0.4 eV and 0.2 eV, respectively, higher compared to the calculations with 14 active electrons. However, the calculations with cc-pVDZ+sp basis set and 10 root are somewhat more reliable than those of the 8 root calculations. The comparison of the excitation energies for 6^1A and 8^1A states of ClOONO suggests that the 8 root calculation obviously treats only one of the 10a $\rightarrow$ 13a / 10a $\rightarrow$ 14a states in the proper way.

The follwing discussion is based on the excitation energies resulted from calculations with 24 active electrons and cc-pVDZ+sp basis set, i.e. bold numbers in Table 2. The SCF-MO energy scheme of ClOONO and BrOONO can be seen from Figure 2. Apparently, the replacement of Cl by Br decreases the HOMO-LUMO energy gap, implying that lower excitation energies can be expected for the bromine analogue in this spectral region. The orbital energy diagram shows a clear separation between 9a and 7a/8a so that one would expect that transitions from 7a/8a lead to higher excited states. Their electronic spectra are illustrated in Figure 3, while in Figure 4 charge density contours of valence and virtual molecular orbitals, which are principally involved in the electronic transitions, are presented.

The lowest excited singlet state of ClOONO, the 1^1A, has a vertical transition energy of 3.18 eV with relatively small oscillator strength of 0.001 and corresponds to the HOMO-LUMO (12a $\rightarrow$ 13a) transition. The low intensity can be explained by transition form an in- plane orbital to one perpendicular to plane. 12a molecular orbital can be considered as to be n(Cl) lone-pair orbital, whereas 13a molecular orbital shows a σ^*(Cl-O) antibonding character. The next two low-energy states at 3.71 eV (12a $\rightarrow$ 14a) and 4.77 eV (11a $\rightarrow$ 13a) are as well single reference and low intensity states. The transition at 5.07 eV (9a $\rightarrow$ 13a) has moderate intensity. 9a molecular orbital shows lone pair non-bonding p-atomic orbital character at chlorine, thus, this transition is related to the n(Cl) $\rightarrow$ σ^*

(O-Cl) type excitation. The f-value obtained form calculations with 14 active electrons is one order of magnitude lower but any difference in the make-up of the wavefunction can be observed. Sizeable oscilator strength, f=0.07, belongs to the electronic excitation computed at 5.18 eV. This 6^1A state corresponds to a linear combination of (10a $\rightarrow$ 13a) and (10a $\rightarrow$ 14a) transitions. By far the strongest transition is found at 5.98 eV with f=0.18 and possesses the complementary character of 6^1A state. 10a $\rightarrow$ 14a can be described as an n(O) $\rightarrow$ π^*(N-O) charge transfer type transition explaining the high intensity. The transition 10a $\rightarrow$ 13a corresponds to a charge transfer from n(O) and σ^* (O-Cl) of 10a to π^*(N-O) of 13a. The last two calculated transitions are located at 6.06 eV and 6.74 eV, the both have low intensity and show multireference character.

An examination of electronic spectra for chlorine and bromine peroxynitrites in Table 2 shows that all low-lying electronic transitions of bromine analogue are lower in vertical excitation energies by about 0.6 - 1.4 eV compared to chlorine analogue. The calculated electronic transition for the first singlet excited state of BrOONO (2.58 eV) is 0.6 eV lower in energy than that for ClOONO (3.18 eV), thus, the transition is blue-shifted by 90 nm when bromine is replaced by chlorine. The dominant vertical excitation energies, 8^1A state, for BrOONO is calculated at 5.19 eV what is about 0.8 eV lower in energy with regard to ClOONO (5.89 eV) or blue-shifted by 32 nm. In contrast to ClOONO (5.07 eV) the 9a $\rightarrow$ 13a transition in BrOONO (3.96 eV) has markedly low intensity. 6^1A states of BrOONO is similar in intensity and in character to that of ClOONO, i.e. moderate intensity and multi-reference character of wavefunction, representing linear combination of 10a $\rightarrow$ 13a and 10a $\rightarrow$ 14a. This transition is blue-shifted by 42 nm when bromine substitues chlorine in peroxynitrite. Finally, we can note that all most important excited states have the multi-reference character of wavefunction, thus multi-reference methods are necessary for studing of halogen peroxynitrite excited states.

On the basis of these calculations, it becomes evident that the very strong UV band at around 210 nm and the somewhat less intense band at around 240 nm would support the ClOONO isomer. For comparison, the dominant electronic transitions of $ClONO_2$ species appear at around 162 nm and 173 nm [31]. Similarly, well separated electronic excitations

are predicted for BrOONO and $BrONO_2$. For BrOONO the strong band is expected at around 240 nm accompanied with less intense band at around 280 nm, while $BrONO_2$ is characterized with very strong band at around 163 nm and strong band at around 176 nm [31].

The present work suggests the following atmospheric implication. In comparison to ClOONO, BrOONO comprises more low-lying excited states that are accessible to the solar radiation where significant actinic flux exists throughout the lower stratosphere, thus the photolysis of BrOONO could be its removal route. These states are all singlet excited states up to 5^1A and all triplet states up to 6^3A for BrOONO, while for ClOONO there are two singlet and three triplet low-lying excited states. However, the dominant electronic excitation of ClOONO falls into the wavelength of atmospheric window.

4. Conclusion

The low-lying singlet and triplet excited states of ClOONO and BrOONO were investigated at MRD-CI level of theory with double- and triple-zeta correlation consistent basis sets. When the calculated electronic transition related to the first singlet excited state of ClOONO (3.18 eV) and BrOONO (2.58 eV) are compared, it is seen that the transition in the chlorine analogue lies 0.6 eV higher than in the bromine compound, i. e., the transition is red-shifted by 80 nm from ClOONO upon replacement of chlorine by bromine. This HOMO $\rightarrow$ LUMO transition can be considered as a n(Cl/Br) $\rightarrow \sigma^*$ (O-Cl/Br) type and is less intense. The red shift from Cl to Br happens due to the fact that the non-bonding valence Br electrons are more loosely bound compared to those of Cl and hence it takes less energy to excite them.

The dominant transitions in the electronic spectra of ClOONO and BrOONO are located at 5.98 eV and 5.19 eV, respectively, with strong intensity and at 5.18 eV and 4.42 eV, respectively, with moderate intensity. Both transitions show multi-reference character, corresponding to linear combinations of the n(O) $\rightarrow \pi^*$ (N-O) type and n(O), σ^*(Cl/Br-O) $\rightarrow \pi^*$(N-O) type transitions. For ClOONO also the excitation at 5.07 eV is calculated

with sizeable intensity and it is related to the n(Cl) $\rightarrow \sigma^*$ (O-Cl) type transition.

Our results provide the informations for identification of XOONO (X = Cl, Br) using the UV-Vis spectroscopic approaches. We have shown that BrOONO comprises more low-lying excited states available for the solar radiation where significant actinic flux exists throughout the lower stratosphere.

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Table 1. Parameters for DIESEL Calculations.

	ClOONO		BrOONO	
BS: cc-pVDZ+sp, Active e^-: 24, Root: 10 Summation threshold: 0.85				
Multiplicity	1		1	
Selection threshold of T	5×10^{-8}		5×10^{-8}	
Reference configurations	198		145	
GC/CSFs [a]	52559365		23352004	
CSFs [b]	2915757		2131360	
BS: cc-pVDZ+sp, Active e^-: 14, Root: 8 Summation threshold: 0.85				
Multiplicity	1	3	1	3
Selection threshold of T:	10^{-7}	10^{-7}	10^{-7}	10^{-7}
Reference configurations	66	49	53	38
GC/CSFs [a]	3339264	5049077	1597656	2137564
CSFs [b]	534706	678341	351621	429496
BS: cc-pVTZ+sp, Active e^-: 14, Root: 8 Summation threshold: 0.85				
Multiplicity	1		1	
Selection threshold of T:	5×10^{-8}		10^{-8}	
Reference configurations	60		57	
GC/CSFs [a]	31208342		27709343	
CSFs [b]	5379615		4703810	

[a] Generated configurations.

[b] Configuration state functions selected.

Table 2. Calculated Vertical Excitation Energies ΔE(eV) and Oscillator Strengths f.

		ClOONO			BrOONO		
State	Excitation	ΔE	f	ΔE_{trip} [a]	ΔE	f	ΔE_{trip} [a]
1^1A	$(12a)^2$ [b]	0.00			0.00		
2^1A	12a → 13a	**3.18** [c]	**0.001**		**2.58**	**0.0002**	
		3.23 [d]	0.001	2.50	2.65	0.0004	2.07
		3.28 [e]	*0.001*		*2.57*	*0.0002*	
3^1A	12a → 14a	**3.71**	**0.0003**		**3.16**	**0.0007**	
		3.76	0.0005	2.99	3.33	0.0005	2.77
		3.79	*0.0008*		*3.32*	*0.0007*	
4^1A	11a → 13 a	**4.77**	**0.002**		**3.77**	**0.003**	
		4.61	0.001	3.81	3.52	0.0005	2.92
		4.55	*0.001*		*3.54*	*0.001*	
5^1A	9a → 13a	**5.07**	**0.01**		**3.96**	**0.0005**	
		5.20	0 .0008	4.83	4.12	0.0007	3.79
		5.21	*0.0009*		*4.09*	*0.0006*	
6^1A	10a → 13a	**5.18**	**0.07**		**4.42**	**0.08**	
	10a → 14a						
		5.41	0.05	4.05			4.16
		5.52	*0.08*		*4.47*	*0.06*	
7^1A	$(11a)^2(13a)^2$	**5.43**	**0.001**		**4.58**	**0.002**	
		5.44	0.003				
		5.51	*0.001*				
8^1A	10a → 14a	**5.98**	**0.18**		**5.19**	**0.22**	
	10a → 13a						
9^1A	9a → 14a	**6.06**	**0.0004**		**5.31**	**0.007**	
	11a → 14a						
		5.63	0.0008	5.19	5.00	0.0006	4.94
		5.74	*0.0007*		*4.94*	*0.0004*	
10^1A	11a → 14a	**6.74**	**0.0003**		**5.35**	**0.001**	
	9a → 14a						

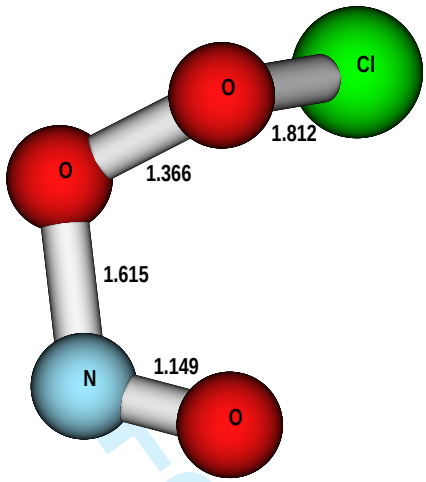
[a] ΔE_{trip} is excitation energy of corresponding triplet transitions relative to the ground state 1^1A energy.

[b] ground state electron configuration: (core)(1-15)a^2 (see text for the explanation of labeling).

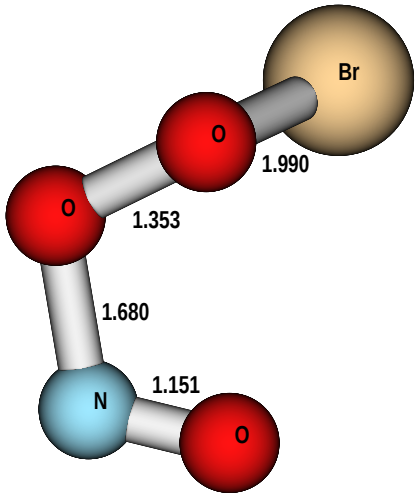
[c] number in bold are related to the calculations with cc-pVDZ+sp basis set, 24 active electrons, 10 roots.

[d] number in roman are related to the calculations with cc-pVDZ+sp basis set, 14 active electrons, 8 roots. The ground state configuration is $(7a)^2$, denotation of excitations corresponds to the number subtracted by 5 in regard to the excitation with 24 active electrons.

[e] number in italic are related to the calculations with cc-pVTZ+sp basis set, 14 active electrons, 8 roots.



∠(ONO) =111.5^0
∠(NOO) =108.0^0
∠(OOCl) =110.5^0
τ(ONOO) = -3.3^0
τ(NOOCl) = 90.6^0



∠(ONO) =109.6^0
∠(NOO) =105.9^0
∠(OOBr) =111.5^0
τ(ONOO) = -3.5^0
τ(NOOBr) = 88.9^0

Figure 1. CCSD(T)/6-311G(d) geometry of ClOONO and CCSD(T)/cc-pVDZ geometry of BrOONO; the bond lengths are given in Å.

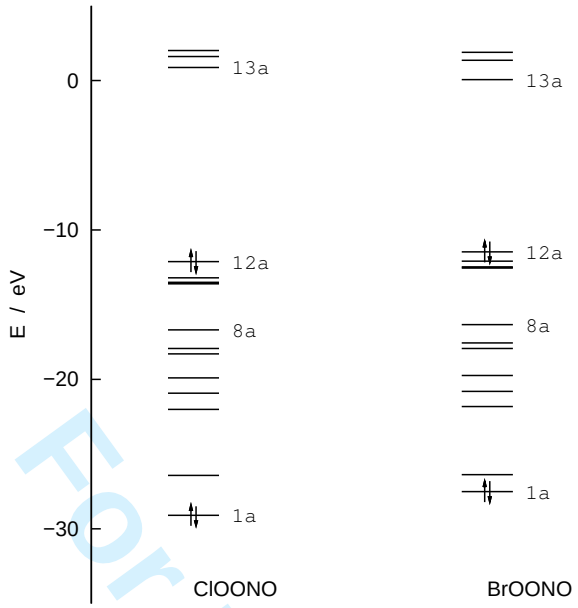


Figure 2. Schematic diagram of the MO energy spectra of the ground state, SCF level (1a to 12 MO's are all double occupied).

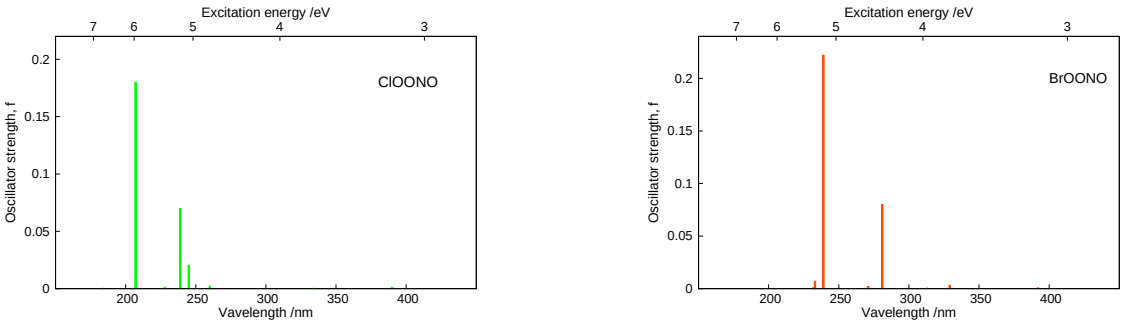
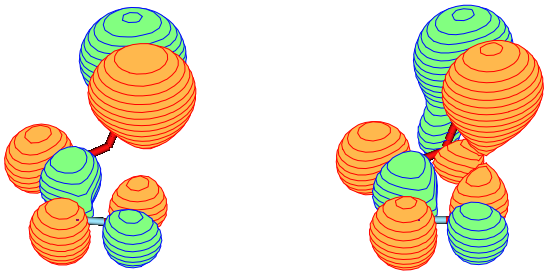
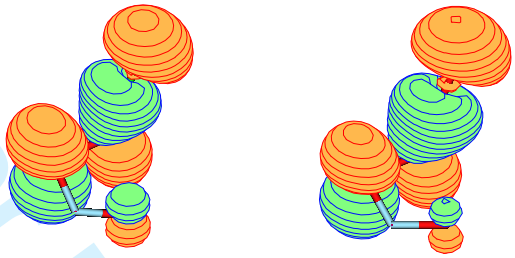


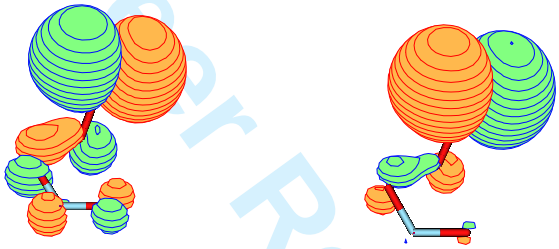
Figure 3. Calculated electronic spectra of ClOONO and BrOONO.



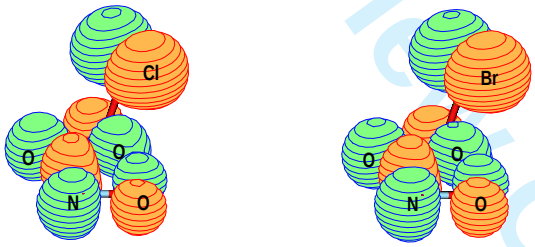
9a



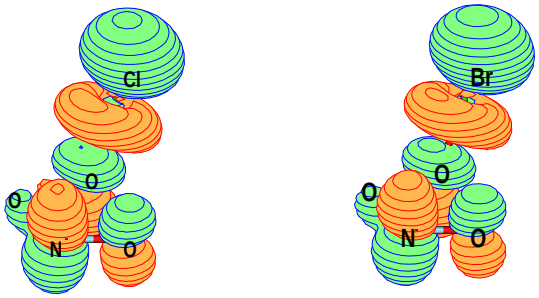
10a



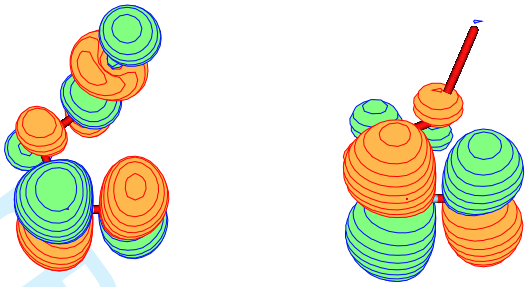
11a



12a, HOMO



13a, LUMO



14a

ClOONO BrOONO

Figure 4. Charge density contours of the highest occupied molecular orbitals (9a, 10a, 11a, 12a) and the lowest unoccupied molecular orbitals (13a, 14a).