

## Computational Study of the Molecular Structure, Vibrational Spectra and Energetics of the OIO Cation

Sang Yeon Lee

Department of Applied Chemistry, Kyungpook National University, Daegu 702-701, Korea

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Molecular geometries for the cationic and neutral species of OXO (X=Cl, Br, and I) are optimized using the Hartree-Fock (HF) theory, the second order Moller-Plesset perturbation theory (MP2), the density functional theory with the B3LYP hybrid functional (B3LYP), and the coupled cluster theory using single and double excitation with a perturbational treatment of triplet excitation (CCSD(T)) methods, with two basis sets of triple zeta plus polarization quality. The single point calculations for these species are performed at the CCSD(T,Full) level. The harmonic vibrational frequencies for these species are calculated at the HF, MP2, B3LYP and CCSD(T) levels. The adiabatic ionization potential for OIO is calculated to be 936.7 kJ/mol at the CCSD(T,Full) level and the correct value is estimated to be around 945.4 kJ/mol.

**Key Words :** Halogen dioxides, Ionization potential, Vibrational frequency, *Ab initio* MO calculation

### Introduction

Although iodine oxides have been known for more than 100 years, their chemistry has not been received much attention until these days.<sup>1</sup> As it is known that the F, Cl, and Br atoms and their oxides play an important role in the ozone depletion in the stratosphere and that the efficiency of the heavier halogen atoms in the ozone depletion has been estimated to be larger than that of the lighter halogen atoms,<sup>2</sup> the role of iodine and iodine oxides in the atmosphere is interesting because they are expected to be more effective in the ozone decomposition. The investigation of iodine chemistry in the atmosphere discovers that iodine species are implicated in the ozone decomposition in the troposphere and lower stratosphere and they are involved in aerosol formation in the marine boundary layer.<sup>3-5</sup> Although many experiments and theoretical studies have been performed in order to understand iodine chemistry in the atmosphere, chemical and physical data for iodine oxides are very scarce. Among the iodine oxides known to be involved in the atmospheric processes, only OI is well characterized.

The next simplest iodine oxide, OIO, is known to be involved in the ozone depletion and is considered to serve as the starting point for the formation of iodine aerosols in the marine boundary layer.<sup>3,5</sup> Miller and Cohen reported the molecular structure of OIO in the ground state derived from its rotational spectrum.<sup>6</sup> The vibrational frequencies for the ground state of OIO have been reported from the vibrational spectra for species in the matrix isolation experiment, the photoelectron spectra of the OIO anion and the absorption spectra of OIO.<sup>7-9</sup> Himmelmann *et al.* and Ashworth *et al.* have reported the absorption spectrum of OIO in the ground state.<sup>9,10</sup> There, however, is no direct experimental determination of the enthalpy of formation for OIO except the upper

limit,  $\Delta_f H_{298}^\circ < 135$  kJ/mol which was derived by Bedjanian *et al.*<sup>11</sup> The photoionization mass spectroscopic method has been successfully applied in determining the enthalpies of formation for simple molecules such as OBrO.<sup>12</sup> Before this technique can be employed in studies determining the energetic properties of OIO, knowledge of the adiabatic ionization potential would be useful.

In this work, the Hartree-Fock theory, the second order Moller-Plesset perturbation theory, the density functional theory with the B3LYP hybrid functional, and the coupled cluster theory using single and double excitation with a perturbational treatment of triplet excitation methods are employed to calculate the adiabatic ionization potential for OIO.

### Calculations

All calculations were performed with the Gaussian 98 program suite.<sup>13</sup> Molecular structures of the neutral and cation species of OXO (X=Cl, Br, and I) are optimized using the Hartree-Fock theory, the second order Moller-Plesset perturbation theory, the density functional theory with the B3LYP hybrid functional, and the coupled cluster theory using single and double excitation with a perturbational treatment of triplet excitation methods. The single point energy calculations were performed at the CCSD(T,Full) level at the geometries optimized with the CCSD(T) method to account for the effects of core-valence correlation. All calculations were performed using two different basis sets of triple-zeta plus polarization quality or better. The first set is 6-311+G(3df) for all atoms.<sup>14,15</sup> This basis set is denoted as AE because all electrons are treated in the calculations explicitly. The second set utilizes the 7 valence electron relativistic effective core potentials developed by Christiansen *et al.* for Br and I atoms.<sup>16</sup> The associated basis functions for Br and I atom developed by Lee were used.<sup>17</sup> The basis functions for Br and I atom were consisted of the (7s7p3d2f)

\*e-mail: sanglee@knu.ac.kr

primitive Gaussian functions and were contracted to the (4s4p3d2f) set. For other atoms except for Br and I atom, the 6-311+G(3df) basis set were employed. This basis set is denoted as ECP to indicate that only the valence electrons for the Br and I atoms are treated explicitly.

The total energy for each molecular species was corrected by the zero-point vibrational energy (ZPVE). For diatomic molecules,  $ZPVE = (\omega_e/2) - (\omega_e x_e/4)$ . For polyatomic molecules,  $ZPVE = 1/2 \sum_i \omega_i + 1/4 \sum_{i,j} \chi_{ij}$ . When experimental vibrational frequencies are not available, the harmonic vibrational frequencies calculated at the level of B3LYP/AE are used.

## Results and Discussion

The optimized molecular structures for the cationic and neutral species of OIO are listed in Table 1. The experimental equilibrium geometry of OIO is included for comparison.<sup>6</sup> Miller and Cohen recorded the rotational spectra of OIO and derived the  $r_0$  structure from the spectra which is used to estimate the equilibrium structure,  $r_e$ .

The OIO in the ground state has  $C_{2v}$  symmetry. The I-O bond length of OIO optimized at the HF/AE level is smaller than the experimental value by 0.042 Å but the O-I-O bond angle deviates only  $-0.7^\circ$  from the experimental value. As the calculation method is changed to better methods such as MP2, B3LYP, CCSD(T), the optimized I-O bond length increases by 0.052-0.062 Å, so that the agreements between the calculated and experimental values improve significantly. The deviations of the bond length from the experimental value are 0.010, 0.018, and 0.016 Å for MP2, B3LYP, and CCSD(T), respectively. The HF method underestimates the bond length by 0.042 Å but all other methods overestimate the bond length by more than 0.01 Å.

As the AE basis is changed to the ECP basis, the optimized I-O bond length decreases by 0.013-0.020 Å, so that the agreements between the calculated and experimental values improve significantly. The O-I-O angle, however, shows

very small changes that are less than  $1.0^\circ$ . This contraction of the bond length originates from the inclusion of scalar relativistic effects through the effective core potential for the I atom. The large change in the bond lengths, upon the inclusion of scalar relativistic effect, stresses that they are not negligible in molecular structures for compounds containing iodine or heavier atoms and thus, should be included in the calculations, at least, in the geometry optimization. The deviations of the optimized bond lengths from the experimental value are  $-0.059$ ,  $-0.003$ ,  $0.002$  and  $0.004$  Å for HF, MP2, B3LYP, and CCSD(T), respectively. Although the MP2 bond length is slightly shorter than the experimental value and the bond lengths obtained at the B3LYP and CCSD(T) levels are slightly larger than the experimental value, all three bond lengths should be regarded as being equivalent.

The OIO<sup>-</sup> turns out to possess  $C_{2v}$  symmetry. As OIO is ionized to form OIO<sup>+</sup>, the I-O bond lengths are optimized at all levels with both basis sets being shortened. The bond angle widens very slightly. The contraction in the bond length means that the I-O bond in the OIO<sup>+</sup> ground state become stronger than the bond in the neutral species. The sizes of the bond contractions depend on the calculation method employed. The contractions in the bond lengths calculated with the AE basis are 0.053, 0.008, 0.046 and 0.028 Å for the HF, MP2, B3LYP and CCSD(T) methods, respectively. The bond contractions calculated with the ECP basis are very similar to those of the AE basis. The contraction in the MP2 bond length is exceptionally small compared to those obtained with the other methods. Thus, the relative order in the optimized bond lengths is changed from MP2 < B3LYP < CCSD(T) for the neutral species to B3LYP < CCSD(T) < MP2 for the ionized species. Since there is no experimental molecular structure for OIO<sup>+</sup> available for comparison with the optimized structures, it is impossible to know which one among the MP2, B3LYP and CCSD(T) methods gives the best results for OIO<sup>+</sup>. But since the CCSD(T) method is the most sophisticated one for the inclusion of electron correlation and is expected to provide the most accurate calculated results, the CCSD(T) result can be regarded as the most accurate. At the CCSD(T)/ECP level, the I-O bond length contracted by 0.030 Å and the bond angle widened by  $0.1^\circ$  upon the removal of an electron from OIO to form OIO<sup>-</sup>.

The harmonic vibrational frequencies for both species calculated using the ECP basis set are listed in Table 2 along with the experimental ones for OIO.<sup>7,8</sup> The first point to note is that although the geometries optimized with the MP2, B3LYP and CCSD(T) methods for OIO are very similar in quality, the harmonic vibrational frequencies calculated with the four methods are very different. The agreements between the calculated and experimental data improved in the order of HF < MP2 < B3LYP < CCSD(T). This pattern is in correlation with the pattern observed in the calculated vibrational frequencies for many molecules.

Consider the harmonic vibrational frequencies calculated for OIO<sup>+</sup>. Since there is no experimental data available for

**Table 1.** The Optimized and Experimental Molecular Structures<sup>a</sup> of OIO and OIO<sup>+</sup>

	AE		ECP	
	O-I	O-I-O	O-I	O-I-O
OIO				
HF	1.758	109.1	1.741	109.6
MP2	1.810	111.1	1.797	111.1
B3LYP	1.818	110.4	1.802	109.9
CCSD(T)	1.816	110.6	1.804	110.8
Exp. <sup>b</sup> ( $r_0$ )	1.805	109.9	1.805	109.9
Exp. <sup>b</sup> ( $r_e$ )	1.800	109.8	1.800	109.8
OIO <sup>+</sup>				
HF	1.706	111.2	1.686	110.8
MP2	1.802	111.5	1.789	111.2
B3LYP	1.772	110.1	1.753	110.2
CCSD(T)	1.789	111.0	1.774	110.9

<sup>a</sup>The bond length in Å and the bond angles in degrees. <sup>b</sup>From ref. 6.

**Table 2.** The Calculated<sup>a</sup> and Experimental Vibrational Frequencies (cm<sup>-1</sup>) for OIO and OIO<sup>+</sup>

Mode	HF	MP2	B3LYP	CCSD(T)	Exp.
OIO					
OIO Bend	333	274	271	267	250 <sup>b</sup>
IO Sym. str.	911	841	787	775	768 <sup>c</sup>
IO Asym. str.	961	873	803	802	800 <sup>c</sup>
OIO <sup>+</sup>					
OIO Bend	365	274	298	281	
IO Sym. str.	1052	810	876	792	
IO Asym. str.	1098	880	909	831	

<sup>a</sup>The calculated vibrational frequencies are obtained using the ECP basis.<sup>b</sup>From ref. 9. <sup>c</sup>From ref. 8.

comparison with the calculated values, the harmonic vibrational frequencies calculated with the CCSD(T) method are chosen to be a reference for comparison with the other calculated values because the CCSD(T) method is known to be the most sophisticated one among the methods employed in the present study in the treatment of electron correlation, provides the best results for OIO, and thus, is expected to give the best results for OIO<sup>+</sup>. The vibrational frequency for the I-O asymmetric stretching is in the order of HF > B3LYP > MP2 > CCSD(T). There is a switch in the positions of the MP2 and B3LYP results compared to the order observed in the calculated vibrational frequencies of OIO. This pattern is also observed for the I-O symmetric stretching and the O-I-O bending mode. When the MP2 and B3LYP frequencies are compared with the CCSD(T) frequencies, it is revealed that the quality of B3LYP frequencies for OIO<sup>+</sup> becomes worse than that for OIO. This deterioration may be related to the known problem in the B3LYP results: the poor description of long range interaction in B3LYP functional. This problem seems to operate more intensively for the ionic compound such as OIO<sup>+</sup>. This phenomenon needs to be examined more closely.

Besides the vibrational frequencies calculated using the MP2 method, the harmonic vibrational frequencies of the neutral species are shifted to the blue as the species is ionized. The shifts in the calculated frequencies obtained with the CCSD(T) method are 14, 17, and 28 cm<sup>-1</sup> for the O-I-O bending, the I-O symmetric stretching and the I-O asymmetric stretching modes, respectively. These shifts indicate that the IO bonds are stronger in OIO<sup>+</sup> than in OIO.

This is consistent with the change in bond lengths calculated for OIO<sup>+</sup>

The zero-point vibrational energy corrected adiabatic ionization potentials (AIPs) calculated for the OXO (X=Cl, Br, and I) are listed in Table 3 along with the experimental AIP values of OCIO and OBrO.<sup>18-21</sup>

Since the experimental value is available for OCIO and OBrO, consider the calculated AIPs for OCIO and OBrO first. The AIPs calculated at the HF and B3LYP levels overestimate the experimental value of OCIO by 22 and 44 kJ/mol, respectively. Those at the MP2 and CCSD(T) levels underestimate it by 44 and 7 kJ/mol, respectively. The inclusion of some core-valence correlation in the CCSD(T) result, that is, the change from the CCSD(T) to the CCSD(T,Full) method, deteriorates the agreement between the calculated and experimental AIPs of OCIO by 0.9 kJ/mol. The deviation of the CCSD(T,Full) result for OCIO from the experimental value is only -7.6 kJ/mol, showing an excellent agreement between the calculated and experimental values. The pattern observed among the AIPs of OBrO is similar to that for OCIO. The inclusion of some core-valence correlation, however, improves the calculated AIP by 0.7 kJ/mol. The influence of the basis set change from the AE to the ECP basis sets for the calculated AIP is negligible. The deviation of the average of AIPs calculated with the CCSD(T,Full) method for OBrO from the corresponding experimental value is -9.8 kJ/mol.

The pattern observed in the calculated AIPs for OIO is similar to that for OCIO and OBrO. The AIPs of OIO calculated with the ECP basis set are smaller than the corresponding values obtained with the AE basis by about 4 kJ/mol. Only the MP2 result is an exception to this trend. The difference between the calculation results obtained with both basis sets can be attributed to the inclusion of the scalar relativistic effect through the effective core potential of the I atom. Since the core-valence correlation effects on the AIPs of OXO (X=Cl, Br, and I) calculated at the CCSD(T)/AE level are less than 1.0 kJ/mol, and thus, the relativistic effect on the AIP of OIO is expected to be more important than the core-valence correlation missed in the ECP calculation for OIO, the AIP of OIO calculated with the ECP basis is expected to be better than the AIP calculated with the AE basis. There is no adiabatic ionization potential reported for OIO. The AIP calculated at the CCSD(T,Full)/ECP level is 936.7 kJ/mol. Since the error of this value is expected to be

**Table 3.** The Calculated and Experimental Adiabatic Ionization Potentials (kJ/mol) for OXO (X = Cl, Br, and I)

Species	Basis Sets	HF	MP2	B3LYP	CCSD(T)	CCSD(T,Full)	Exp.
OCIO	AE	1018.7	953.0	1040.7	990.2	989.1	996.7 ± 1.9 <sup>a</sup>
OBrO	AE	1042.0	935.3	1039.0	982.2	982.9	992.8 ± 2.9 <sup>b</sup>
	ECP	1042.1	934.7	1036.4	982.5	983.0	
	Average		935.0	1038.1	982.4	983.0	
OIO	AE	999.1	898.6	988.7	940.3	940.1	945.4 <sup>c</sup>
	ECP	996.6	889.9	985.3	936.2	936.7	
	Average		894.5	987.1	938.3	938.4	

<sup>a</sup>From ref. 18 and 19. <sup>b</sup>From ref. 20 and 21. <sup>c</sup>The estimated value in the present work.

similar to the corresponding AIPs for OCIO and OBrO, the correct AIP of OIO can be estimated by correcting the average of deviations of the calculated values for OCIO and OBrO from the corresponding experimental values. The estimated value is 945.4 kJ/mol and its uncertainty is expected to be less than 5 kJ/mol.

Let us consider the pattern among AIPs of OXO (X=Cl, Br, and I). As X in OXO is changed from Cl to Br, the AIP decreases 3.9 kJ. If the same amount was changed when X=Br is replaced with X=I, the AIP for OIO would be around 988 kJ/mol. This value, however, deviates from the estimated correct value by 43 kJ/mol. This phenomenon suggests that extrapolating the trend observed in the properties of compounds when the chlorine atom in the compounds is replaced with the bromine atom to the iodine compounds is not a good strategy for estimating the properties of iodine compounds.

### Summary

Molecular geometries for the cationic and neutral species of OXO (X=Cl, Br, and I) are optimized using the HF, MP2, B3LYP and CCSD(T) methods with two basis sets of triple zeta plus polarization quality. The single point calculations for these species are performed at the CCSD(T,Full) level. The harmonic vibrational frequencies for these species are calculated at the HF, MP2, B3LYP and CCSD(T) levels. The adiabatic ionization potential for OIO is calculated to be 936.7 kJ/mol at the CCSD(T,Full) level and the correct value is estimated to be around 945.4 kJ/mol. This was obtained by correcting the calculated value with the average deviation of the calculated adiabatic ionization potentials for OCIO and OBrO from the corresponding experimental data.

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