Asymmetric Halogen Dioxides: High level calculations and Anion Photoelectron Spectroscopy

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Abstract

Gas phase complexes formed between bromide and iodide anions and molecular oxygen are investigated via high level CCSD(T) calculations and experimental anion photoelectron spectroscopy. Experimental electron binding energies of the $^2P_{3/2}$ and $^2P_{1/2}$ states are determined to be 3.43 and 3.90 eV, and 3.12 and 4.06 eV for the bromide and iodide complexes respectively. Calculations predict one minimum for each of the halide-oxygen complexes corresponding to a bent C_s geometry, while for the analogous neutral (radical) complexes two stationary points were located; one linear ($C_{\infty v}$) and another T-shaped (C_{2v}). These lie close in energy to one another ($\Delta E < 1\,\mathrm{kJ\,mol^{-1}}$) suggesting that internal rotation of the oxygen molecule is highly likely.

Keywords:
anion complex, photoelectron spectroscopy, ab initio, halogen, oxygen

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1. Introduction

The role of halogen containing molecules in the catalytic cycle that leads to the depletion of stratospheric ozone was first proposed by Molina in 1974 [1]. Subsequent improvements to the proposed mechanism by Vaida highlighted the role that certain intermediates, for example chlorine dioxides, play in determining the kinetics of this system [2]. A key aspect of the proposed mechanism was the photoisomerisation of the halogen dioxides between symmetric OClO and asymmetric ClOO species.

$$\mathrm{ClO + O_3 \longrightarrow ClOO + O_2}$$
$$\mathrm{ClOO \xrightarrow{M} Cl + O_2}$$
$$\mathrm{Cl + O_3 \longrightarrow ClO + O_2}$$

It is natural, therefore, following the identification of the role of chlorine dioxides that there is also interest in the possible involvement of bromine and iodine dioxide species in the catalytic destruction of ozone, despite their lower stratospheric concentrations compared with the chlorine species [3]. Of course, the largest volume of experimental and theoretical work has been presented for the chlorine containing complexes, and this has been dominated by the symmetric OClO species. In the following discussion, we concentrate on the anion species, particularly seeing that applying anion photoelectron spectroscopy to the anion species allows one to access and provide precise information on important regions of the analogous neutral surface.

Spectra have been recorded for the the $ClOO^-$, $OClO^-$, and ClO^- anions [4, 5]. The most recent work of this kind was performed by Boesl and Distelrath who reported values for all three of the chloride species using anion-ZEKE spectroscopy [4]. In this study, two different gas phase synthetic techniques were employed to produce either the symmetric OClO and ClO species or the asymmetric ClOO species. The electron affinities were reported as 2.2775(13) eV, 2.1451(25) eV and 3.6600(2) eV for ClO, OClO and ClOO, respectively. Of particular interest was the the asymmetric $ClOO^-$ species which was determined to be a weakly bound van der Waals style cluster. This conclusion was based on the similarity of its photoelectron spectrum when compared to that of the bare chloride anion, and on the comparison between electron affinities of ClOO and the similar weakly bound ClAr species (3.6594 eV). The latter was identified as a van der Waals complex prior to the work on $ClOO^-$ [6]. Another compelling piece of evidence was the low vibrational frequencies for the bending and stretching modes determined from the spectra which is indicative of a loosely bound van der Waals complex [4].

Following on from the experimental work [4], Irikura presented a suite of high level calculations on the asymmetric $ClOO^-$ anion complex using CCSD, CCSD(T) and multi configuration methods [7]. According to Irikura, 'The CCSD(T) level is expected to be more reliable than CASSCF or MCQDPT2 for the ground state, since the triplet is well described by a single configuration and CCSD(T) recovers more of the dynamical correlation effects'. The $ClOO^-$ complex was predicted to exist in three forms, being a 'T-shaped' geometry of C_{2v} symmetry ($^3B_1$), a linear geometry of $C_{\infty v}$ symmetry ($^3\Sigma^-$), and a 'bent' geometry of C_s symmetry ($^3A''$). The calculations suggested that the bent complex corresponded to the minimum energy geometry. MCSCF calculations show differences in geometry and energy between the triplet and singlet states of the ClOO neutral complex however the states lie very close to one another in energy, with the singlet state lying only 200 cm^{-1} higher.

Extensive theoretical investigations into the neutral XOO radicals have also been undertaken, and similarly for both the anion and neutral of the symmetric structure, however a search of the literature did not reveal work on the asymmetric anion XOO^-. Alcami [8] reports calculations on the BrOO ($^2A''$) radical, noting that multiple methods fail to agree with one another or previously reported experimental work. These XOO ($^2A''$) radicals have since been revisited by Denis utilising CCSD(T) methods [9, 10] who suggests that due to their multiconfigurational character, two initial solutions to the HF step present themselves. In the case of FOO the spin contaminations are $\langle s^2\rangle = 1.40$ and $\langle s^2\rangle = 0.76$ respectively and while the SCF method will tend to the lower energy solution (here the high spin contamination case), the subsequent CCSD(T) energy is higher by 14.56 $\mathrm{kJ\,mol}^{-1}$ and is shown to differ from both experimental geometries and enthalpies of formation. As such, while CCSD(T) methods seem appropriate for use in calculating the ground triplet state of XOO complexes, multireference methods similar to those used by Irikura[7] are necessary for highly correlated species.

Geometries for both isomers of the BrO_2 radical were determined by Pacios [11] using UMP2 methods and averaged relativistic effective potentials with TZ(2df) basis sets, with subsequent energies determined using CCSD(T) methods. The geometry determined for the BrOO radical show good agreement with some calculations by Alcami, namely those of QCISD(T)/ECT+(2df) and QCISD(T)/ECT(2d) with Br−O distances of 2.290 Å and 2.302 Å, O−O bond lengths of 1.217 Å and 1.232 Å, and Br−O−O angles of 117.2° and 117.4° respectively. While the latter shows less agreement with geometries calculated by Pacios, the accompanying O−O stretching frequency ($1486\,\mathrm{cm}^{-1}$) is consistent with multiple matrix IR experiments that report this value to be typically between $1485\,\mathrm{cm}^{-1}$ and $1487\,\mathrm{cm}^{-1}$ [12, 13, 14, 15, 16, 17]. Similarly NIST-JANAF reference data includes heats of formation for the OBrO radical, the result of CCSD(T) calculations that are in good agreement with experimental data [12]. These methods compare with unrestricted DFT which while able to describe structures reasonably well, greatly overestimates the frequency of the O−O stretch for both ClOO and BrOO [18].

Modest theoretical work using DFT functionals and DZP++ (double zeta plus polarisation and diffuse functions) basis sets has attempted to quantify the electron affinities and vertical detachment energies (VDE) of the BrOO radicals and anion respectively [19]. The anion shows lower vibrational frequencies for both the BYLP and BP86 functionals which is atypical for an anion by comparison to the analogous neutral species and indicative of a van der Waals complex. However calculated geometries vary wildly between functionals and as such the determined VDE of 3.84 eV is taken only as an approximate value.

Numerous analogous computational studies concentrating on iodine dioxide have also been undertaken [20, 21] with representative examples being the work by Misra [22] where optimised geometries were determined via MP2 calculations and the energies of these calculated using QCISD(T) methods. Lee [23] also calculated structures and energies of OIO using CCSD(T) methods. Overall similar structures to the chlorine and bromine species were predicted, albeit with larger bond lengths and angles in the case of iodine. With the addition of work by Peterson [24] studying the isomerisation and dissociation pathways of OIO neutrals to ground state $O_2 + I$ again via a combination of multireference methods and CCSD(T), the understanding of some of these interactions near completion however as of writing there is a sparsity of theoretical work on the triplet neutral and anion IOO.

Experimentally, matrix IR spectra have been recodred for the OIO radical [25] with vibrational frequencies typical of the symmetric species. Additionally, prior photoelectron spectroscopy studies on the symmetric halogen dioxides have recorded electron binding energies for the bromine [26] and iodine [5, 26] species, however to the best of our knowledge photoelectron spectra have not been presented for the asymmetric complexes, XOO^-. In these studies, the synthetic route for the gas phase species involved electrospray ionisation (ESI) of stable ionic species dissolved in solution [26], or rational gas phase synthesis using the flowing afterglow technique [5], neither of which is conducive to the production of the van der Waals style asymmetric $X^{-}\cdots OO$ complex. Again, the only anion photoelectron spectra reported in the literature is for the chloride complex, $ClOO^{-}$ [4].

This work makes a timely contribution to the field by providing experimental and theoretical studies of the asymmetric class of complexes. We present results from ab initio calculations on the BrOO and IOO anions and neutral gas phase complexes. In addition, the first anion photoelectron spectra are presented for these interesting species, thereby providing electron affinities for the asymmetric neutral radical XOO species.

2. Methodology

2.1. Computational Methods

The $X\cdots O_2$ anion and neutral complexes were addressed using the CCSD(T) level of theory with basis sets of triple-ζ quality. Where comparable computational data exists, as is true in the case of ${ClO_2}^{-}$[7] we seek to replicate existing CCSD(T) results. Dunnings augmented correlation consistent basis set was employed for oxygen and fluorine (aug-cc-pVTZ) [27] while basis sets including additional diffuse functions and effective core potentials developed by Peterson et al. were employed for chlorine (aug-cc-pV(T+d)Z)[28] and bromine and iodine atoms (aug-cc-pVTZ PP)[29, 30] respectively.

Various starting geometries were trialled to sample the potential energy surface, and after successful optimisation to a stationary point vibrational frequency analysis was undertaken to test whether the complex corresponded to a minima, transition state, or high order stationary point. Energies of the bare anions, neutral radicals, and bare O_2 were computed in order to determine the cluster binding energy D_e. Harmonic zero point energies of the complexes and bare oxygen were used to determine D_0. In addition, single point energy calculations using up to quintuple-ζ basis sets were employed for a two point complete basis set limit extrapolation along the lines of W1 and W2 theory [31]. All quantum chemical calculations were performed using the CFOUR package [32].

2.2. Experimental Methods

The experimental apparatus consists of an anion time of flight mass spectrometer after the Wiley and McLaren design [33] which is combined with a magnetic bottle photoelectron spectrometer [34]. The design and function of the spectrometer has been described previously [35, 36], and hence only a brief description of the experimental methodology pertaining to the $X^{-}\cdots O_2$ complexes is described here.

The spectroscopic targets were created by intersecting energetic electrons with a pulsed supersonic expansion of a preformed gas mixture, which consisted of oxygen and argon (approximately 1:10 ratio) seeded with traces of CH_3I and CH_2Br_2(halide anion precursors). The total pressure of the gas mixture was 400 kPa.

The $X^{-}\cdots O_2$ clusters were selected using time of flight mass spectrometry and overlapped by a 5 ns pulse of 266 nm radiation (4.66 eV, 4th harmonic of a Nd:YAG laser, Spectra Physics Quanta Ray Pro) while subjected to a strongly divergent magnetic field. The generated photoelectrons are guided to a detector at the end of a 1.5 m flight tube through application of a second homogeneous magnetic field present along the length of the flight tube. The time of flight of the detached photoelectrons with respect to the laser pulse is recorded, converted to kinetic energy (eKE), and subsequently converted to electron binding energy (eBE) via,

$$eBE = h\nu - eKE \tag{1}$$

where $h\nu$ is the energy of the incident photon. An individual spectrum was collected over 10 000 laser shots, with the final spectrum representing the average over several days. Calibration of the spectrometer was achieved by recording the spectra from the bare halide anions, and the intensity corrected for the conversion from time of flight binning to energy binning of the photoelectrons. Further details on this procedure, and the resolution of the spectrometer can be found in reference [36].

3. Results and discussion

3.1. Computational Results

Typical geometries of the XOO anion complexes were predicted using electrostatic interaction models similar to those applied to the XN_2 complexes previously[37]. Geometries of the complexes were defined by the distance from the halide to the midpoint of the O−O bond and the angle formed between the halide, this point and one of the oxygen atoms. These models accounted for charge-quadrupole, charge-hexadecapole and charge-induced dipole interactions utilising parallel and perpendicular polarisabilities of the oxygen molecule. Quadrupole and hexadecapole moments used were taken from calculations performed by Bartolomei[38], while polarisability values of O_2 have been determined as $a_{\|} = 15.01$ au and $a_{\perp} = 8.02$ au (au $\equiv e^2 a_0^2 E_h^{-1}$) respectively.[39] The resulting contour plot with with contour separation of 25 cm^{-1} is presented here in Figure 1, and suggests XO_2^{-} geometries of C_s symmetry with a X−||−O angle of approximately 135°.

While this model is rudimentary it has shown good agreement with the results of CCSD(T) calculations with key results summarised here in Figure 2 (full data is provided in Supplementary Information). An anion C_s minimum belonging to the $^3A''$ state along with neutral C_{2v} and $C_{\infty v}$ minima belonging to the $^4A_1$ and $^4\Sigma^-$ states respectively were calculated. Calculations on the XO_2^{-} complexes predict similarly bent geometries and while $r_{\mathrm{X-O}}$ distances range from 2.864 Å to 3.771 Å they are significantly longer than one would expect from a covalently bound molecule. It should be noted that calculations on the ClO_2^{-} C_s complex agree precisely with those completed previously by Irikura [7]. This distance coupled with the relatively unperturbed oxygen molecule and low complex stabilisation energy (D_0) are strong indicators

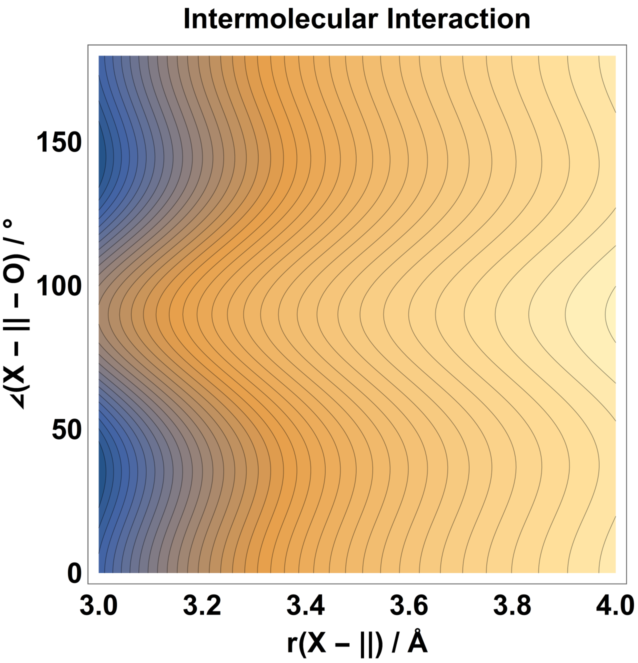

Figure 1: Electrostatic intermolecular interaction determined for anion complexes. Here the halides are represented by a point charge and plot contours are separated by 25 cm^{-1} with blue indicative of stronger interaction.

that the anion geometries belong to vdW complexes. Additional stationary points belonging to the C_{2v} and $C_{\infty v}$ anion complexes have also been located however whereas the C_s geometry has been confirmed to be a minimum via harmonic frequency calculations, these structures represent first and second order transition states with imaginary frequencies in the X−O−O bending mode. Considering that the bending mode in the bent structure is at most 32 cm^{-1} and that the energy separation between this structure and the C_{2v} and $C_{\infty v}$ geometries are all below 1 kJ mol^{-1}, full internal rotation is likely provided a low rotational barrier is present.

Ewing [40] defines vdW molecules based on four different rotational coupling cases; free rotors, weakly coupled, strongly coupled and semi-rigid. While primarily concerned with the rotational spectroscopy of such molecules, the most strongly bound, semi-rigid case offers a conceptual basis for the molecules as symmetric tops. Alongside the C_s symmetry of the XOO anion complexes and low energy differences between the two transition states we are able to suggest they are weakly coupled. Considering the nature of bonding interaction given the bent structures of the anion XOO complexes we have defined these complexes previously with respect to the distance between the halide and midpoint of the oxygen double bond. Given the ionic radii is analogous to the electrostatic charge density, by plotting the ionic radii of the halides from Shannon [41] against these distances from CCSD(T) calculations, we demonstrate near perfect correlation (Figure 3) whereas such a relationship is not present when comparing the ionic radii with the X−O distance.

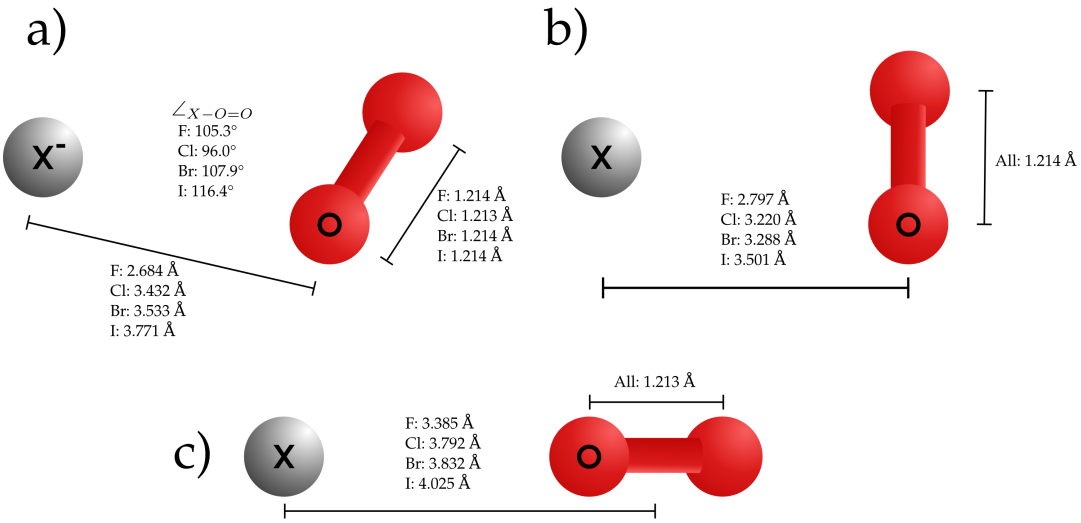

Figure 2: Optimised geometries for the XOO complexes. a) represents the XO_2^- C_s minimum, while b) and c) represent the respective C_{2v} and $C_{\infty v}$ XO_2 minima.

This suggests that previous descriptions of the vdW interaction electrostatic interaction are indeed valid.

While the anion complexes are characterised by ion-multipole interactions the neutral complexes are defined by dispersion forces, more typical of vdW complexes. CCSD(T) calculations predict two minima for each halogen; a T-shaped (C_{2v}) and linear complex ($C_{\infty v}$) with the T-shaped lying lower in energy, the geometries for which are summarised in Figure 2 similarly to the anion. In addition to the geometry optimisation and harmonic frequency calculations, a rotational scan between the T-shaped and linear complexes was completed for the ClOO complex (CCSD(T)/aug-cc-pV(T+d)z), with the Cl−|| and O−O distances optimised at each step (Figure 4). The barrier for internal rotation between the T-shaped minimum the corresponding linear complex was determined to be approximately $0.64\,\mathrm{kJ\,mol^{-1}}$. Given that the zero point energy contributions of the X−O−O bending mode and the X−O stretching mode range from $0.72\,\mathrm{kJ\,mol^{-1}}$ and $1.41\,\mathrm{kJ\,mol^{-1}}$ and assuming that the barriers for internal rotation for the other halogen complexes are similarly small it can be surmised that XOO complexes undergo free internal rotation of the oxygen molecule.

Select computational results from literature are provided here in Table 1. Irikura[7] notes that the Birge-Sponer extrapolation completed in $ClOO^-$ ZEKE spectroscopy work overestimated the D_0 value for the anion complex. While calculations in this work agree with Irikura's value of D_0 for the anion, they overestimate this value for the neutral complex. This is likely due to the use of highly accurate experimental electron affinities in Irikura's calculation whereas the value reported here is determined from calculations only on the neutral state and subsequently do not account for the anharmonicity of the vdW stretching mode. Ultimately characterising the energies of the anion complexes and those corresponding geometries on the neutral surface belonging to the $^4A''$ state allow vertical detachment energies (VDE) to be determined.

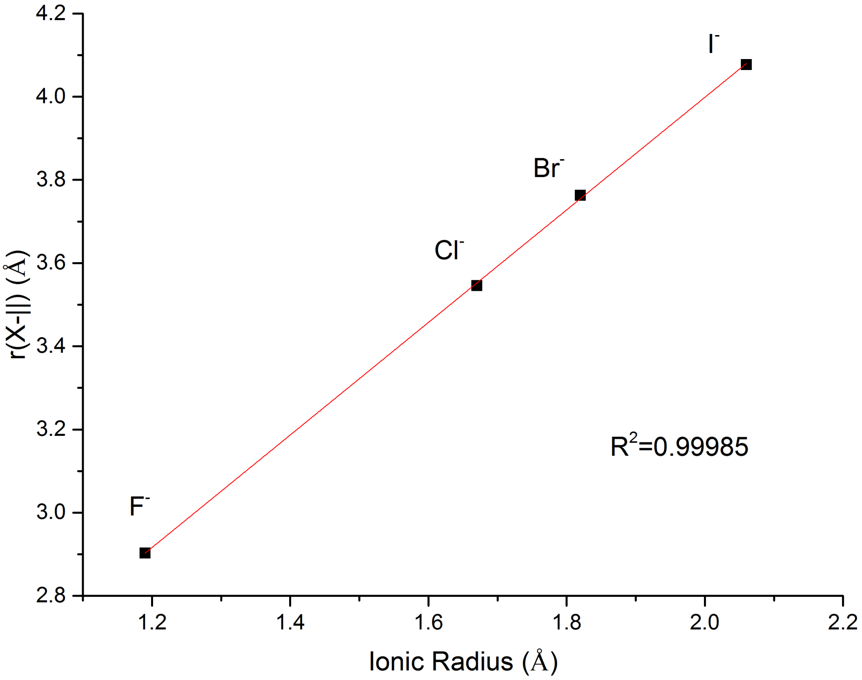

Figure 3: Plot of ionic radii against $X^{-}-||$ distance in the ${XO_2}^{-}$ C_s anion complexes.

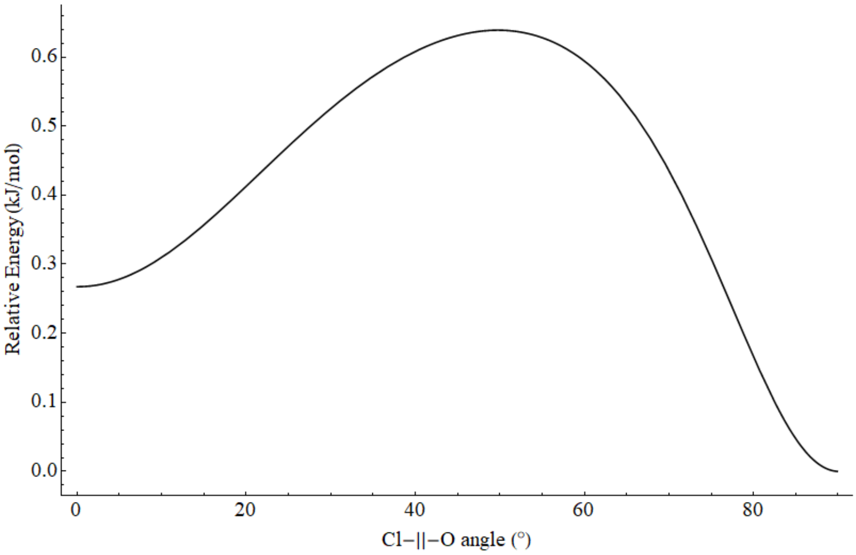

Figure 4: Relaxed rotational scan of the ClOO complex about the Cl−||−O angle.

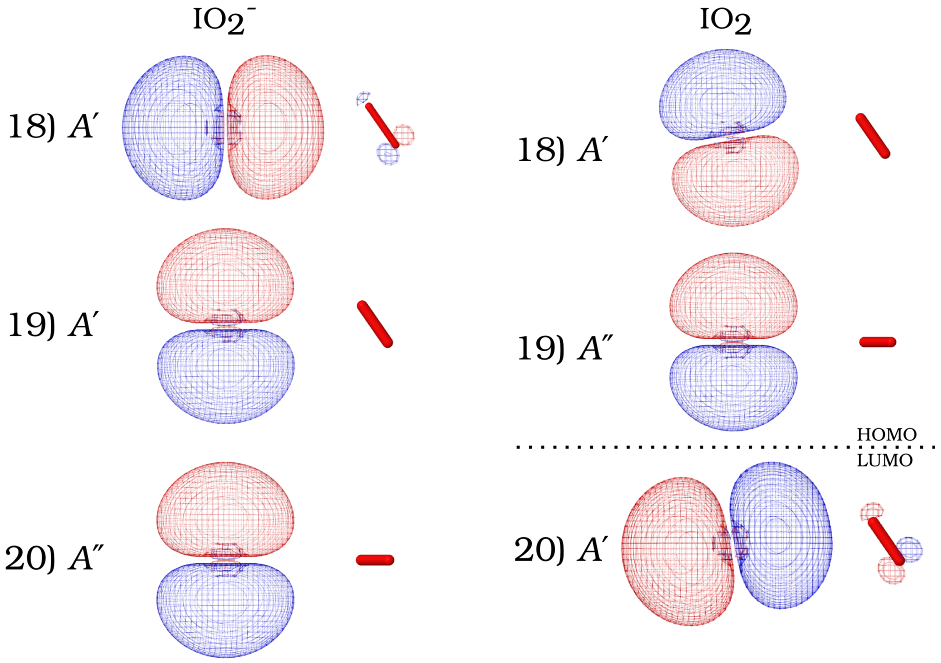

Figure 5: β molecular orbitals (contour value 0.04) calculated from UHF/aug-cc-pVTZ wavefunctions for the IO_2^- and IO_2 complexes. Photodetachment appears to be from number 18 A' orbital.

Plotting the β molecular orbitals (Figure 5) of the IO_2^- $^3A''$ and IO_2 $^4A''$ as a representative example of XO_2^-, the $^3A'' \leftarrow {}^4A''$ transition is the result of photodetachment from a perturbed p-orbital on the halide. Following this, by artificially splitting the predicted VDEs by applying spin-orbit state separations of the bare halogens from reference experimental spectra, peak positions can be predicted which are summarised alongside experimental spectra to follow (Table 1).

Work	Method	Anion D_e	Anion D_0	Neutral D_e	Neutral D_0
Distelrath[4]	Birge-Sponer extrapolation	6.2	6.7	2.2	2.0
Irikura[7]	CCSD(T)	6.2	5.7	-	1.2
This Work	CCSD(T)	6.2	5.7	2.3	1.9

Table 1: Comparison of ClOO neutral and anion complex binding energies between this work and literature (all values are in $\mathrm{kJ\,mol^{-1}}$).

3.2. Experimental Photoelectron spectra

A representative mass spectrum of the dibromomethane seeded oxygen-argon gas mixture is presented here (Figure 6), with $p(O_2) = 30\,\mathrm{kPa}$. From the spectrum, calibrated initially from the pair of bromide-79 and bromide-81 peaks and then additionally from the iodide-126 peak, complexes of bromide-79 with water, nitrogen, oxygen and argon can be seen at mass to charge ratios of 96.88, 106.86, 110.89 and 118.82

respectively. Additionally the triplet of peaks in the region of $m/z = 174$ are due to the $Br^{-}\cdots H_2CBr$ complex, as opposed to the dibromomethane anion this complex is assigned as such based on previous IR studies of such anion-radical complexes[42]. Similarly to the XO_2 anion complexes reported here the $Br^{-}\cdots H_2CBr$ complex is of C_s symmetry and shows a similar bent structure. Utilising the IUPAC[43] definition of mass resolution $R = \frac{M}{\Delta M}$, where M is the peak position and ΔM is the full width half maximum, the resolution of the peaks corresponding to the bromide-79-oxygen complex and the bromide-81-bromomethane-81 complex have calculated resolutions of 245 and 237 respectively. Being some of the lowest intensity peaks present in the mass spectrum both of these show suitable mass separation for subsequent photoelectron spectroscopy.

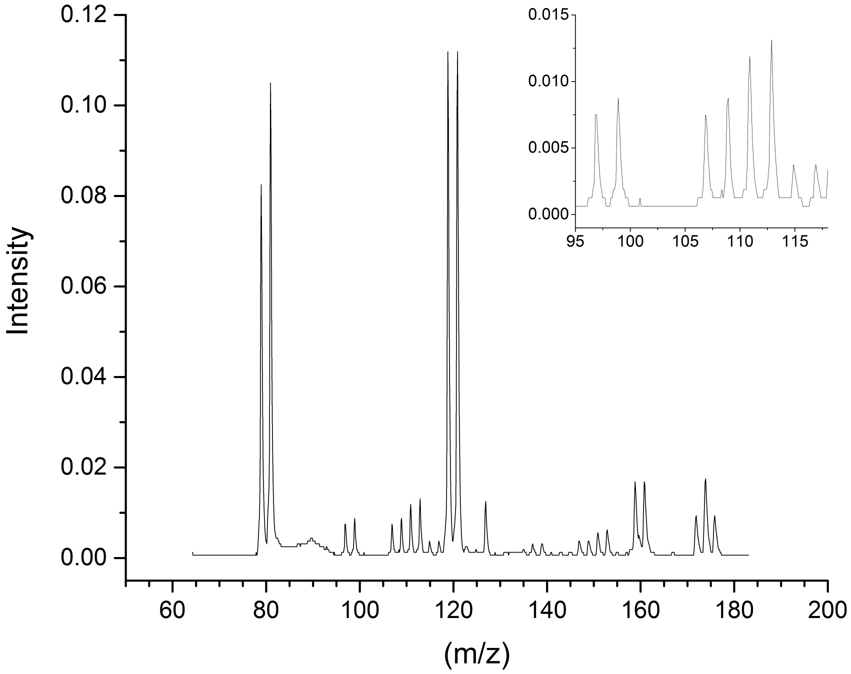

Figure 6: Time of flight mass spectrum of a bromide-oxygen-argon gas mixture.

The anion photoelectron spectra of the $BrOO^{-}$ and IOO^{-} complexes are presented in Figures 7 and 8 with the vertical detachment energies predicted from CCSD(T) calculations presented as overlaid stick spectra. We report the electron binding energies from the anion to the two neutral electronic states (the result of the spin-orbit splitting of the halogen) as 3.43 eV and 3.90 eV for the $BrOO^{-}$ complex and 3.11 eV and 4.06 eV for the analogous iodide complex. The difference between these binding energies with those of the bare halides is then the electron stabilisation energy associated with complex formation and represent the difference in the D_0 values of the anion and neutral complexes. For BrOO these electron stabilisation energies are 0.07 eV and 0.08 eV while for IOO they are 0.05 eV and 0.06 eV. These values are similar for both spin-orbit states and the small difference between them is likely due to the uncertainty associated with the peak assignments of the spectra.

In comparing the calculated vertical detachment energies with those from experiment (both this work and literature[4]) in Table 2, the largest deviation from experiment present is the $^2P_{1/2}$ transition of the BrOO complex. Although the calculated energy difference between the C_s and $C_{\infty v}$ conformers of the BrOO complex is 0.3 kJ mol^{-1} and subsequently this detachment could come from any orientation of the O_2 molecule, the strong agreement between these values is confirmation of detachment of a vdW complex and warrants further higher resolution spectroscopic studies to discern to what degree the oxygen is bound.

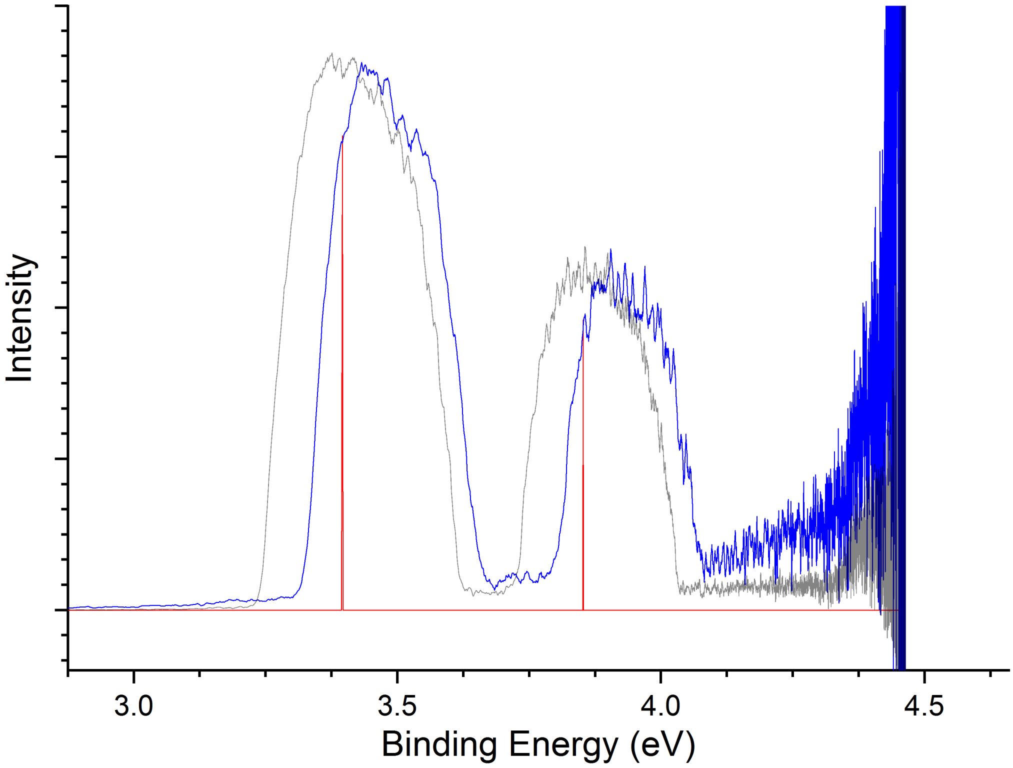

Figure 7: Anion photoelectron spectrum of a) $BrOO^-$ complex (blue trace) and b) Bare Br^- (grey trace), overlain with the CCSD(T)/CBS vertical detachment energies to the ^2P states of the BrOO neutral (red trace). Recorded with photo energy of 4.66 eV.

Along with the peaks due to transitions to the two spin-orbit states of the halogen there is an additional spectral feature present in the IOO anion photoelectron spectrum. While it was considered that this feature might be the result of photodetachment to vibrationally excited states of the O−O stretch in the complex, the calculated vibrational frequency of 1568 cm^{-1} and the energy difference between the $0 \leftarrow 0$

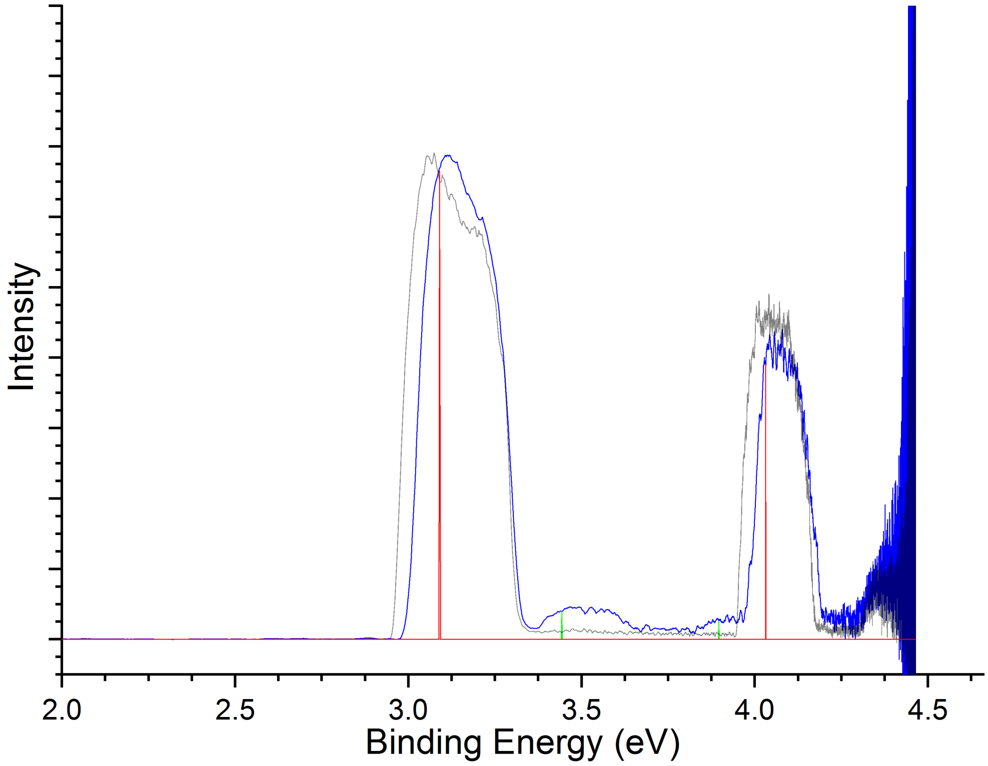

Figure 8: Anion photoelectron spectrum of a) IOO^- complex (blue trace) and b) Bare I^- (grey trace), overlain with the CCSD(T)/CBS vertical detachment energies to the ${}^2P$ states of the IOO neutral (red trace). Also included is the contaminant stick spectrum of the co-temporal ${BrAr_2}^-$ from Yourshaw[45] (green trace). Recorded with photo energy of 4.66 eV.

and this peak being approximately 3000 cm^{-1} make this unlikely. In the process of this investigation a photoelectron spectrum was simulated using CCSD(T)/CBS energies and vibrational frequencies from the aug-cc-pvtz calculation using ezSpectrum[44]. Given the geometry change between the C_s anion and C_{2v} neutral is significant, Franck-Condon factors were determined using Duschinsky rotations. However as the mode descriptions of the C_s anion appear difficult to assign, the normal modes between the two states are significantly non-parallel and the determinant of the rotation matrix S is 0.0128 suggesting poor overlap between the two.

Inspecting the mass spectrum of the iodide-oxygen-argon gas mixture, a small peak is present with a m/z ratio of 160.9. Given that this mass could correspond to a $Ar_2 \cdots {}^{81}Br^-$ complex it is suspected that the corresponding bromide-79 complex may be contaminating the IOO photoelectron spectrum. Consulting previous work by Yourshaw[45] the binding energies of the two ${}^2P$ states of $Ar_2 \cdots {}^{81}Br^-$ complex are 3.443 eV and 3.897 eV. The $Ar_2 \cdots Br$ ${}^2P_{3/2}$ transition corresponds well to the unassigned structure in the spectrum and the ${}^2P_{1/2}$ transition also corresponds to structure on the leading edge of the IOO ${}^2P_{1/2}$ peak allowing assignment of both spectral structures.

3.2.1. Comparisons

Complex	Computational Method	$D0_{anion} \| D0_{neut}$ kJ mol^{-1}	$^2P_{3/2_{Exp}} \| ^2P_{3/2_{Comp}}$ eV	$^2P_{1/2_{Exp}} \| ^2P_{1/2_{Comp}}$ eV
$\mathrm{F\cdots O_2}$	CCSD(T)/CBS	9.8|0.6	-|3.50	-|3.55
$\mathrm{F\cdots N_2}$[a]	CCSD(T)/CBS	15.7|0.6	-|-	-|-
$\mathrm{Cl\cdots O_2}$[b]	CCSD(T)/CBS	5.7|1.9	3.66|3.66	3.77|3.77
$\mathrm{Cl\cdots N_2}$[c]	CCSD(T)/CBS	8.5|1.1	3.72|3.69	3.83|3.80
$\mathrm{Cl\cdots CO}$[d]	UMP2/aug-cc-pVQZ PP	3.5|1.7	3.83|3.79	-|-
$\mathrm{Br\cdots O_2}$	CCSD(T)/CBS	5.3|2.4	3.43|3.40	3.90|3.85
$\mathrm{Br\cdots N_2}$[a]	CCSD(T)/CBS	7.8|3.5	3.42|3.41	3.92|3.86
$\mathrm{Br\cdots CO}$[e]	CCSD(T)/aug-cc-pVTZ PP	9.9|3.5	3.50|3.42	3.97|3.87
$\mathrm{I\cdots O_2}$	CCSD(T)/CBS	5.2|3.8	3.12|3.09	4.06|4.03
$\mathrm{I\cdots N_2}$[a]	CCSD(T)/CBS	7.0|5.0	3.07|3.08	3.92|4.02
$\mathrm{I\cdots CO}$[f]	CCSD(T)/aug-cc-pVTZ PP	7.3|3.2	3.16|3.11	4.11|4.06

[a] Ref [37]

[b] Experimental values are from Ref [4] while computational values are from this work

[c] Ref [46]

[d] Separation of ^2P states completed in Ref [46] was not completed here

[e] Ref [47]

[f] Ref [48]

Table 2: Vertical detachment energies and complex stabilisation energies for various halide-molecule complexes, reported to 3 significant figures for consistency.

By comparison with other halide-molecule complexes (namely XN_2 complexes) the halide-oxygen complexes are typically less strongly bound in both the anion and neutral cases, likely due to the differences in polarisability between the oxygen and nitrogen molecules. Both oxygen and nitrogen complexes display similar trends in complex stabilisation energy across the halides and halogens with D_0 decreasing for the anion and increasing for the neutral as F→I. Similar to the differences in halogen-molecule pairs being the result of the polarisability of the molecules, these halogen trends correlate with the polarisability of the halogen while the decrease in complex stability in the anion is related to the single point charge density of the anion through its effective ionic volume.

Considering the XCO complexes there are present similar bonding motifs in the anion complexes with C_s structures present, again indicative of the dominance of the charge induced multipole interaction. Conversely due to the permanent dipole of the CO molecule the corresponding neutral complexes tend towards linear geometries whereas in the nitrogen and oxygen complexes these geometries are of C_{2v} symmetry which as noted is due to the polarisability of the triple and double bond being greater orthogonally than parallel.

4. Summary

Experimental photoelectron spectra of the halide-oxygen complexes have been recorded. These spectra demonstrate a shift to higher electron binding energy indicative of an increase in the complex stabilisation energy on going from the neutral to the analogous anion complex. Accompanying experimental data are the results of CCSD(T) geometry optimisation and harmonic frequency calculations with energies extrapolated to the complete basis set limit. These calculations indicate minima for the anion complex as a bent structure and linear and T-shaped structures for the neutral complexes and allow the prediction of vertical detachment energies that agree very well with experimental data. Using the chlorine complexes as an example the barrier for internal rotation of the oxygen molecule suggests that while these structures are regions of potential they ultimately emphasise the classification of these complexes as very loosely bound, with a calculated barrier height in the neutral of approximately $0.64\,\mathrm{kJ\,mol^{-1}}$. Additional spectral features present in the $\mathrm{IOO^-}$ spectrum have been assigned to transitions to the ^2P states of the contaminating $\mathrm{Ar_2Br^-}$ complex.

5. Acknowledgements

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6. Bibliography

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