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# On the Spectroscopic and Thermochemical Properties of ClO, BrO, IO, and Their Anions

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A coupled cluster composite approach has been used to accurately determine the spectroscopic constants, bond dissociation energies, and heats of formation for the $X_1{}^2\Pi_{3/2}$ states of the halogen oxides ClO, BrO, and IO, as well as their negative ions $ClO^-$, $BrO^-$, and $IO^-$. After determining the frozen core, complete basis set (CBS) limit CCSD(T) values, corrections were added for core−valence correlation, relativistic effects (scalar and spin−orbit), the pseudopotential approximation (BrO and IO), iterative connected triple excitations (CCSDT), and iterative quadruples (CCSDTQ). The final *ab initio* equilibrium bond lengths and harmonic frequencies for ClO and BrO differ from their accurate experimental values by an average of just 0.0005 Å and 0.8 $cm^{-1}$, respectively. The bond length of IO is overestimated by 0.0047 Å, presumably due to an underestimation of molecular spin−orbit coupling effects. Spectroscopic constants for the spin−orbit excited $X_2{}^2\Pi_{1/2}$ states are also reported for each species. The predicted bond lengths and harmonic frequencies for the closed-shell anions are expected to be accurate to within about 0.001 Å and 2 $cm^{-1}$, respectively. The dissociation energies of the radicals have been determined by both direct calculation and through use of negative ion thermochemical cycles, which made use of a small amount of accurate experimental data. The resulting values of $D_0$, 63.5, 55.8, and 54.2 kcal/mol for ClO, BrO, and IO, respectively, are the most accurate *ab initio* values to date, and those for ClO and BrO differ from their experimental values by just 0.1 kcal/mol. These dissociation energies lead to heats of formation, $\Delta H_f$ (298 K), of 24.2 ± 0.3, 29.6 ± 0.4, and 29.9 ± 0.6 kcal/mol for ClO, BrO, and IO, respectively. Also, the final calculated electron affinities are all within 0.2 kcal/mol of their experimental values. Improved pseudopotential parameters for the iodine atom are also reported, together with revised correlation consistent basis sets for this atom.

## I. Introduction

The importance of the halogen oxides ClO, BrO, and IO in atmospheric catalytic ozone depletion chemistry, particularly in the stratosphere,[1] has motivated numerous high level experimental and theoretical studies on these species. In the cases of the BrO and IO radicals, these species represent about 40 and 90% of inorganic bromine and iodine, respectively, in the stratosphere. High-resolution spectroscopy studies have led to very accurate determinations of the molecular constants in the $X_1{}^2\Pi_{3/2}$ ground states of all three radicals (refs 2−10 and references therein) whereas studies of the near-ultraviolet $A_1{}^2\Pi_{3/2}-X_1{}^2\Pi_{3/2}$ electronic transitions of ClO and BrO have led to accurate values of their ground state dissociation energies and heats of formation.[11−13] A reliable spectroscopic determination of the IO dissociation energy has yet to be reported, and hence its value has more experimental uncertainty than its chlorine or bromine analogs.

The halogen oxides are known to be challenging species to describe with ab initio electronic structure methods. Accurate results require high levels of electron correlation, either by coupled cluster or multireference configuration interaction methods, as well as large 1-particle basis sets and inclusion of relativistic effects. Because of the availability of a nearly complete set of accurate molecular constants for all three species, these molecules provide a unique set of benchmark systems involving isovalent open shell radicals between three rows of the periodic table. In the present work, all three radicals are treated at the same level of theory using a systematic coupled cluster composite method[14−19] that attempts to account for all major sources of error in an ab initio calculation.

To provide more insight into the resulting accuracy of the neutral radical results, analogous calculations have also been carried out on the closed-shell halogen oxide anions. Far fewer experimental and theoretical studies have been previously carried out on these species, with most studies focusing on the accurate determination of the halogen oxide electron affinities.[20−29] The present work provides the most accurate predictions for the spectroscopic constants of these species to this date, as well as a secondary route for the calculation of the neutral dissociation energies.

## II. Computational Methods

The base set of calculations on both the radicals and anions involved a frozen core, coupled cluster singles and doubles calculation with a perturbative treatment of connected triples, CCSD(T).[30,31] The open shell calculations utilized the RHF−UCCSD(T) variant, i.e., R/UCCSD(T), and were based on restricted open-shell Hartree−Fock (ROHF) orbitals.[32−36] The orbitals in the atomic calculations were fully symmetry equiva-

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**TABLE 1: Coefficients *B* and Exponents $\beta$ of the Modified MCDHF-Adjusted Energy-consistent Small-core Pseudopotential of Iodine**

| $l$ | $j$ | $B$ | $\beta$ |
|---|---|---|---|
| s | 1/2 | 49.9896493 | 40.0333763 |
| | | 281.0065555 | 17.3005763 |
| | | 61.4167387 | 8.8517200 |
| p | 1/2 | 202.2487177 | 15.7201414 |
| | | 43.6996443 | 8.2941863 |
| p | 3/2 | 202.2115434 | 15.2082222 |
| | | 43.4526325 | 7.7539491 |
| d | 3/2 | 88.8468904 | 13.8177514 |
| | | 24.2911651 | 6.9476304 |
| d | 5/2 | 88.8995986 | 13.5878054 |
| | | 24.9624997 | 6.9600987 |
| f | 5/2 | −47.0787756 | 18.5229504 |
| | | −0.5143463 | 7.5579010 |
| f | 7/2 | −45.6541352 | 18.2510351 |
| | | −0.3878806 | 7.5974040 |

lenced. These CCSD(T) calculations employed a series of three correlation consistent basis sets ranging from triple- to quintuple-$\zeta$, namely aug-cc-pV*n*Z for oxygen,[37,38] aug-cc-pV($n$+$d$)Z for chlorine,[39,40] and aug-cc-pV*n*Z-PP for bromine[41] and iodine, where $n$ = T, Q, and 5. Relativistic Douglas-Kroll-Hess (DKH) contracted versions of the O and Cl basis sets were used for ClO/ClO$^-$ because the DKH Hamiltonian[42,43] was used throughout in these cases. The aug-cc-pV*n*Z-PP basis sets for Br and I included small-core energy-consistent relativistic pseudopotentials (PP), cf. below. In the following, these basis sets will be collectively referred to as aV*n*Z where $n$ = T, Q, 5.

The Br (1s−2p) and I (1s−3d) inner cores were replaced by energy-consistent pseudopotentials that were optimized in multiconfigurational Dirac−Hartree−Fock calculations. The parameters of the Br PP were taken from ref 41, whereas a modified version of the iodine PP of ref 41 was used in the present work. The modification of the iodine PP was motivated by the fact that molecular bond lengths for HI and $I_2$ were significantly underestimated in ref 41 (by 0.0025 and 0.0055 Å, respectively) with respect to corresponding DKH all-electron calculations, while the deviations for the Br and At compounds were much smaller (less than 0.0002 and 0.001 Å, respectively). To improve the fit of the iodine PP of ref 41, which was done to atomic total valence energies, we first removed all explicit reference to the inner core, i.e., we replaced the total valence energies (differences between energies of ground and excited states of near-neutral atoms, on the one hand, and the energy of the highly charged inner core, on the other hand) by energy differences between the aforementioned states of near-neutral atoms.[44] Second, we replaced the information on the inner core by data for outer-core excitations that might help to improve the performance of the PP; specifically, we included the $4s^1 4p^6 4d^{10} 5s^2 5p^6$, $4s^2 4p^5 4d^{10} 5s^2 5p^6$, and $4s^2 4p^6 4d^9 5s^2 5p^6$ configurations within the least-squares fit of the PP parameters. The resulting deterioration of the total valence energies was very moderate (0.7%), whereas the energy differences of the states of the valence spectrum were significantly improved. The maximum error of configurational averages is reduced by about 1 order of magnitude (from 0.02 to 0.003 eV), and also the maximum error of individual relativistic states becomes slightly smaller (0.05 instead of 0.06 eV). Also, it was possible to reduce the number of terms in the *d* projector of the potential from 3 to 2 per ($l$, $j$) combination, without loss of accuracy. The parameters of the modified iodine PP are listed in Table 1. New correlation consistent basis sets, which have the same composition as those of ref 41, have been optimized for these new PP parameters. Using the new PP parameters and basis sets, the CCSD(T)/ cc-pV5Z-PP equilibrium bond lengths of HI and $I_2$ are now underestimated by just 0.0006 and 0.0011 Å, respectively, compared to analogous DKH calculations.

For the molecules of the present work, calculations were carried out at a total of 7 bond distances unequally distributed around the approximate equilibrium geometries of each species ($r - r_e = -0.3, -0.2, -0.1, 0.0, +0.1, +0.3, +0.5\ a_o$) and the resulting energies were fit to sixth-order polynomials in displacement coordinates. The fitted coefficients were then used in subsequent Dunham analyses.[45] To exploit the systematic basis set convergence characteristics of the correlation consistent basis sets, the total energies at each bond length were extrapolated to the complete basis set (CBS) limit using[46−48]

$$E(n) = E_{\mathrm{CBS}} + B\mathrm{e}^{-(n-1)} + C\mathrm{e}^{-(n-1)^2} \quad (n = 3, 4, 5) \qquad (1)$$

and

$$E(n) = E_{\mathrm{CBS}} + B/n^3 \quad (n = 4, 5) \qquad (2)$$

where $E_{\mathrm{CBS}}$ is the resulting CBS limit and $n$ refers to the cardinal number of the correlation consistent basis set (2 = DZ, 3 = TZ, etc.). The best CBS estimate was taken as the average of these two results, and the spread was accepted as an estimate of the uncertainty in the extrapolation procedure.[15] The CBS energies were then fit and subjected to the same Dunham analysis as above. Extrapolation of the total energies rather than treating the Hartree−Fock (HF) and correlation energies separately, particularly in regards to eq 2, is purely a matter of convenience in the present work. With basis sets of QZ and 5Z quality, the basis set truncation error for the correlation energy far exceeds that of the HF contribution. Nevertheless this assumption was tested for the case of IO, whereby only the correlation energies (QZ, 5Z) were extrapolated via eq 2, and these results were added to the HF energies calculated with the aug-cc-pV5Z-PP basis set. The resulting spectroscopic constants and dissociation energy were within the uncertainties obtained from applying eqs 1 and 2 to the total energies, which were typically about ±0.001 Å, ±1 cm$^{-1}$, and ±0.2 kcal/mol for $r_e$, $\omega_e$, and $D_e$, respectively, for the molecules of this study.

The contributions to the total energies due to core−valence correlation, namely 1s for O, 2s2p for Cl, 3s3p3d for Br, and 4s4p4d for I, were calculated at the CCSD(T) level of theory with core−valence basis sets of quadruple-$\zeta$ quality, aug-cc-pwCVQZ for O and Cl (ref 49) and aug-cc-pwCVQZ-PP for Br and I.[50] The DKH-contracted versions of the Cl and O basis sets were used in the cases of ClO/ClO$^-$. In all cases, the core-valence basis sets were used in both valence-only and all-electrons correlated calculations, and the difference in energies defined the total core-valence correction. It should be noted that the 1s electrons of Cl are never correlated in these calculations.

The second contribution to the CCSD(T)/CBS energies was specific to BrO/BrO$^-$ and IO/IO$^-$ and was designed to correct both for the pseudopotential approximation and the scalar relativistic effects due to oxygen in these molecules. In this case, correlated DKH CCSD(T) calculations were carried out using DKH-contracted, all-electron aug-cc-pwCVTZ basis sets,[51,52] and the resulting spectroscopic constants were compared to those from analogous PP-based calculations using aug-cc-pwCVTZ-PP basis sets[50] on Br and I (with the standard aug-cc-pwCVTZ set[49] on O).

The effects due to molecular and atomic spin−orbit coupling were recovered by use of the double-group spin−orbit configuration interaction (SO−CI) method[53] as implemented in the Columbus program suite.[54] In these calculations, the spin−orbit parameters accompanying the pseudopotentials described above were used throughout, and accurate PPs were also used on both the chlorine[55] and oxygen[56] atoms. The aug-cc-pVTZ-PP basis sets were employed on Br and I, whereas the aug-cc-pVTZ basis sets recontracted in the presence of the PPs were used for Cl and O. The SO correction was defined by the difference in two calculations, a full valence, complete active space (CAS) reference, multireference singles and doubles CI (MRCISD) calculation that did not include the spin−orbit operator and an analogous MRCISD that mixed (via the spin−orbit operator) either doublet and quartet states in the case of the neutral radicals or singlet and triplet states for the closed-shell anions. In each case, CASSCF orbitals were used and only the valence electrons were correlated. Analogous calculations were also carried out for all of the atomic species of this work. This procedure differed slightly from other recent work from our laboratory[16] where CISD natural orbitals were used in conjunction with MRCIS calculations. The final results, however, differed only slightly, e.g., by less than 0.1 kcal/mol for the spin−orbit correction to $D_e$ for IO.

The last correction was for the effects of higher electron correlation beyond the CCSD(T) level of theory. The differences between perturbative and full iterative connected triple excitations,[57−60] $E_{CCSDT} - E_{CCSD(T)}$, were calculated with the aug-cc-pVTZ basis sets (−DK for ClO/ClO$^-$, standard and −PP for BrO/BrO$^-$ and IO/IO$^-$), whereas the effects of iterative connected quadruples,[57,61−63] $E_{CCSDTQ} - E_{CCSDT}$, employed the analogous double-ζ basis sets. A total of 5 bond distances were sampled in each case for each species, the CCSD(T) $r_e$ obtained with the specified basis set (DZ or TZ) and displacements from this value of −0.04, −0.02, +0.02, and +0.04 $a_o$. The CCSD(T), CCSDT, and CCSDTQ potential curves were then fit to cubic polynomials to determine the minimum energies, equilibrium bond lengths, and harmonic frequencies. Last, estimates of the full configuration interaction (FCI) results were obtained with the aug-cc-pVDZ basis sets by carrying out continued fraction (cf) extrapolations[15,64] with the CCSD, CCSDT, and CCSDTQ energies, i.e.,

$$E_{FCI,cf} = \frac{E_{CCSD}}{1 - \frac{\left(\frac{\delta_T}{E_{CCSD}}\right)}{\left(1 - \frac{\delta_Q}{\delta_T}\right)}} \tag{3}$$

where $\delta_T = E_{CCSDT} - E_{CCSD}$ and $\delta_Q = E_{CCSDTQ} - E_{CCSDT}$. All of the CCSD(T) calculations of this work were carried out with the MOLPRO suite of ab initio programs.[65] The CCSDT and CCSDTQ calculations were carried out primarily with the string-based MRCC program of Kállay[66] as interfaced to MOLPRO. The CCSDT calculations on ClO were performed with the NWChem program.[67,68]

### III. Results

The calculated results for the $X_1{}^2\Pi_{3/2}$ states of ClO, BrO, and IO are shown in Table 2 where they are also compared to the available experimental data. Only modest changes in $r_e$ and $\omega_e$ are observed between the aV5Z basis set and the CBS limit, however the effect of the basis set extrapolation on $D_e$ is as high as 0.83 kcal/mol for BrO. Core−valence correlation is calculated to have a minor impact on the dissociation energies, but it yields relatively large bond length shortenings, especially for IO where $r_e$ decreases by 0.0092 Å upon 4s4p4d electron correlation. As expected, the inclusion of spin−orbit coupling increases in importance from ClO to IO. The effects of SO coupling on $D_e$ shown in Table 2 are significantly different from what one might estimate based only on the experimental zero-field splittings. This is due to strong second-order effects, especially for IO. Of particular interest in Table 2 are the contributions of iterative triple and quadruple excitations in the coupled cluster treatment compared to CCSD(T). The difference between CCSDT and CCSD(T), $\Delta T$, is relatively large due to the not insubstantial amount of nondynamical correlation in these molecules as indicated by the somewhat large $T_1$ diagnostics, which run as large as about 0.07 for IO. In each case, iterative triples increase the bond lengths by about 0.003 Å, decrease the harmonic frequencies, and increase the dissociation energies, the latter by 0.10 to 0.57 kcal/mol. In regards to the equilibrium bond lengths, the effects of iterative connected quadruple excitations, $\Delta Q$, are small, less than 0.001 Å. Their effect on the dissociation energies, however, is substantial, ranging from +0.56 to +0.70 kcal/mol. The contributions for IO are slightly different from those reported previously[16] due to the different bond lengths used and new PP. It should be particularly noted that in each case, the iterative triples and quadruples corrections are both in the same direction compared to the CCSD(T) results, i.e., they both increase the dissociation energies over the CCSD(T) values and, hence, a fortuitous cancellation of the CCSDT−CCSD(T) and CCSDTQ−CCSDT contributions does not occur in these cases as is often observed (see, e.g., the results for IBr in ref 16). Finally, the effects of correlation beyond CCSDTQ, as estimated by the continued fraction approximation, are small and amount to only about 0.1 kcal/mol for $D_e$ and are essentially negligible for $r_e$ and $\omega_e$. The final results for the spectroscopic constants of ClO and BrO are in excellent agreement with experiment − within 0.001 Å for $r_e$, 1.5 cm$^{-1}$ for $\omega_e$, and about 0.1 kcal/mol for $D_e$. The final calculated $r_e$ for IO, 1.8723 Å, is 0.0047 Å longer than experiment while $\omega_e$ is larger by just 1.9 cm$^{-1}$. This calculated value for $r_e$ is a little longer than our recently reported value[16] due to the different PP used in this work and the effects of iterative triples and quadruples of the present work. The current discrepancy with experiment for $r_e$ is presumably due to the underestimation of spin−orbit coupling effects. The present calculations yield a bond length shortening due to spin−orbit coupling of 0.0057 Å, however the value estimated from experiment (determined as one-half the difference in bond lengths between the $\Omega$=3/2 and 1/2 states) would correspond to a SO correction of −0.0086 Å. This additional −0.003 Å would bring our ab initio result to within 0.001 Å of experiment.

To obtain further insight into the accuracy of the current SO calculations, the excited $X_2{}^2\Pi_{1/2}$ state of each radical has also been investigated. These results are shown in Table 3 where they are compared to the accurate experimental values. The equilibrium state separation is reproduced to with 2% (9 cm$^{-1}$) for ClO, but it is underestimated for BrO and IO by about 12−15%. The shifts in the equilibrium bond lengths and harmonic frequencies between the two components, however, is very well reproduced in all three cases. In fact, the excellent agreement between theory and experiment for $\Delta r_e$ of IO contrasts the calculated SO correction for $r_e$ in the $X_1{}^2\Pi_{3/2}$ state, which as mentioned above was presumably too small. The origin of this apparent inconsistency is currently not clear. Additional calculations on both SO states of IO were also carried out that included correlation of the 4p and 4d electrons of iodine at the MRCIS level (with appropriate extension of the I basis set with a 2p2d2f set of core-valence functions from the cc-pwCVTZ-PP basis). Including this extra contribution of core correlation, however,

**TABLE 2: Contributions and Final Predicted Values for Equilibrium Bond Lengths (Å), Harmonic Frequencies (cm$^{-1}$), and Dissociation Energies (kcal/mol) of the $X_1{}^2\Pi_{3/2}$ States of $^{35}$ClO, $^{79}$BrO, and $^{127}$IO with Comparison to Experiment[a]**

| | CCSD(T)/aV5Z | ΔCBS | ΔCV | ΔSO | ΔDK | ΔT | ΔQ | ΔFCI | Total | expt.[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| ClO | | | | | | | | | | |
| $r_e$ | 1.5711 | −0.0029 | −0.0033 | −0.0007 | − | 0.0031 | 0.0009 | 0.0001 | 1.5683 | 1.5689 |
| $\omega_e$ | 856.6 | 3.8 | 3.6 | 2.2 | − | −6.5 | −2.6 | −0.3 | 856.7 | 855.5 |
| $D_e$ | 63.58 | 0.83 | 0.06 | −0.61 | − | 0.10 | 0.56 | 0.06 | 64.60 | 64.65(1) |
| BrO | | | | | | | | | | |
| $r_e$ | 1.7220 | −0.0024 | −0.0043 | −0.0026 | 0.0000 | 0.0032 | 0.0008 | 0.0001 | 1.7168 | 1.7172 |
| $\omega_e$ | 729.7 | 3.2 | 3.6 | 4.7 | −0.7 | −4.5 | −2.3 | −0.3 | 733.4 | 732.9 |
| $D_e$ | 57.31 | 0.68 | −0.05 | −2.05 | −0.10 | 0.32 | 0.60 | 0.07 | 56.77 | 56.9(1) |
| IO | | | | | | | | | | |
| $r_e$ | 1.8859 | −0.0031 | −0.0092 | −0.0057 | 0.0010 | 0.0029 | 0.0004 | 0.0000 | 1.8723 | 1.8676 |
| $\omega_e$ | 670.1 | 2.3 | 5.7 | 9.0 | −1.2 | −1.3 | −0.9 | −0.1 | 683.6 | 681.7 |
| $D_e$ | 56.57 | 0.67 | 0.13 | −3.35 | −0.17 | 0.57 | 0.70 | 0.09 | 55.20 | |

[a] The best predicted values are given under the column "Total" and are equal to CCSD(T)/aV5Z + ΔCBS + ΔCV + ΔSO + ΔDK + Δ*T* + Δ*Q* + ΔFCI; ΔCBS = difference between CCSD(T) CBS and aV5Z values, ΔCV = core-valence correlation correction obtained with aug-cc-pwCVQZ (awCVQZ) basis sets, ΔSO = contribution from molecular and atomic spin−orbit coupling, ΔDK = difference between all-electron DKH CCSD(T)/awCVTZ calculations and pseudopotential-based CCSD(T)/awCVTZ with all-electrons correlated (not shown for ClO because the DK Hamiltonian was used throughout, except for the SO calculations), Δ*T* = difference between CCSDT and CCSD(T) results with aVTZ, Δ*Q* = difference between CCSDTQ and CCSDT results with aVDZ. The FCI correction, ΔFCI, was calculated by extrapolating the CCSD, CCSDT, and CCSDTQ energies (aVDZ basis) using the continued fraction approximation (see text). [b] References 3, 4, 10, and references therein. See Table 5 for a number of experimental $D_0$ values for IO.

**TABLE 3: Calculated Values for the Spin−orbit Constants ($A_e$, cm$^{-1}$), Shifts in the Equilibrium Bond Lengths ($\Delta r_e$, Å), and Harmonic Frequencies ($\Delta\omega_e$, cm$^{-1}$) Relative to the $X_1{}^2\Pi_{3/2}$ States for the $X_2{}^2\Pi_{1/2}$ States of ClO, BrO, and IO with Comparison to Experiment**

| | $A_e$ | $\Delta r_e$ | $\Delta\omega_e$ |
|---|---|---|---|
| ClO | | | |
| theory (this work) | −313 | +0.0014 | −4.1 |
| expt.[3] | −321.96 | +0.00121 | −3.3 |
| BrO | | | |
| theory (this work) | −856 | +0.0066 | −13.3 |
| expt.[4] | −975.43 | +0.00684 | −14.9 |
| IO | | | |
| theory (this work)[a] | −1775 | +0.0175 | −32.2 |
| expt.[10,23] | −2091(40) | +0.01706 | −36.4 |

[a] These values change to −1827 cm$^{-1}$, +0.0177 Å, and −33.0 cm$^{-1}$, respectively, with the inclusion of core correlation in the spin−orbit calculations. See the text.

while increasing the spin−orbit constant $A_e$ by 52 cm$^{-1}$ led to only negligible changes in the other spectroscopic constants compared to the valence-only results (see Table 3). It should also be noted that pseudopotential-based SO calculations have also previously been carried out on IO at the multireference configuration interaction (MRCI) level of theory by Roszak et al.[69] using basis sets of triple-ζ quality. Their results are in good semiquantitative agreement with the present values for the spectroscopic constants in the $X_1{}^2\Pi_{3/2}$ and $X_2{}^2\Pi_{1/2}$ states.

Coupled cluster results for the spectroscopic constants of the halogen oxide anions are shown in Table 4 where they are also compared to the available experimental values. The magnitudes of the basis set extrapolation and core−valence correlation contributions are observed to be very similar to those calculated for the neutral radicals. Not surprisingly, the effects due to spin−orbit coupling are relatively small for these closed-shell species, except of course for the electron affinity, which involves the open-shell radicals. It is very interesting to note the effects of iterative triple and quadruple excitations on the CCSD(T) spectroscopic constants and energetics. For the equilibrium bond lengths and harmonic frequencies, the Δ*T* and Δ*Q* corrections both have the same sign, just as in the case of the neutrals, but the iterative triples correction for $r_e$ is an order of magnitude smaller than Δ*Q*, which reflects the relatively small $T_1$ diagnostics for the anions and hence higher accuracy of the perturbative triples approximation. The effects of iterative quadruples on the bond lengths, +0.002 to +0.003 Å, are rather larger than expected, but recent work in our laboratory on the isovalent BrCl molecule yielded a nearly identical correction.[70] In contrast to the neutral radicals, the iterative triples and quadruples corrections to CCSD(T) for the dissociation energies are opposite in sign for the anions. Although these two terms do not completely cancel, they do result in relatively small overall corrections (∼0.3 kcal/mol) to the CCSD(T) results. In the case of the electron affinities, the effects of iterative triples dominate the correlation corrections to the CCSD(T) results, amounting to −0.6 to −1.0 kcal/mol. The final ab initio values for $r_e$ and $\omega_e$ of the negative ions are all within the relatively large error bars of the values derived from photoelectron spectroscopy.[23,24] Based on our results for the neutral radicals, as well as other related systems, the final ab initio results [CCSD(T)/aV5Z + ΔCBS + ΔCV + ΔSO + ΔDK + Δ*T* + Δ*Q* + ΔFCI] have uncertainties of about 0.001 Å and 2 cm$^{-1}$ for $r_e$ and $\omega_e$, respectively. The dissociation energies and electron affinities shown in Table 4 are in excellent agreement with experiment, exhibiting deviations from the accurate experimental values of just 0.1−0.2 kcal/mol. The present results for ClO$^-$ and BrO$^-$ are also in very good agreement with the previous coupled cluster calculations of Kim et al.[25] and Francisco et al.,[22] respectively. The calculations of Kim et al., which included correlation up through CCSDT with CBS extrapolations, yields a nearly identical electron affinity for ClO as the present work after molecular spin−orbit corrections are added to their result.

Table 5 summarizes the dissociation energies and resulting heats of formation calculated in the present work compared to experiment for the neutral halogen monoxide radicals. The ab initio dissociation energies have been derived using two schemes, (a) by direct calculation as given in Table 2 and (b) via the negative ion thermochemical cycle

$$D_0(\mathrm{XO}) = D_0(\mathrm{XO}^-) + \mathrm{EA}(\mathrm{X}) - \mathrm{EA}(\mathrm{XO}) \quad (\mathrm{X{=}Cl, Br, I}) \tag{4}$$

where the electron affinities were taken from the accurate experimental results.[21,23,24,71,72] While it is our belief that the

**TABLE 4: Contributions and Final Predicted Values for Equilibrium Bond Lengths (Å), Harmonic Frequencies ($cm^{-1}$), Dissociation Energies (kcal/mol), and Electron Affinities (kcal/mol) of the $X^1\Sigma^+$ States of $^{35}ClO^-$, $^{79}BrO^-$, and $^{127}IO^-$ with Comparison to Experiment**[a]

| | CCSD(T)/aV5Z | ΔCBS | ΔCV | ΔSO | ΔDK | ΔT | ΔQ | ΔFCI | Total | expt.[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $ClO^-$ | | | | | |
| $r_e$ | 1.6835 | −0.0036 | −0.0036 | 0.0000 | − | +0.0007 | +0.0025 | +0.0004 | 1.6798 | 1.673(8) |
| $\omega_e$ | 667.2 | +3.3 | +2.4 | 0.0 | − | −1.5 | −2.5 | −0.2 | 668.6 | 665(25) |
| $D_e$ | 32.71 | +0.64 | +0.13 | −0.15 | − | −0.33 | +0.61 | +0.07 | 33.68 | 33.60(4) |
| $EA_e$ | 52.75 | +0.33 | −0.08 | −0.47 | − | −0.57 | +0.15 | +0.02 | 52.12 | 52.26(3) |
| | | | | | $BrO^-$ | | | | | |
| $r_e$ | 1.8131 | −0.0030 | −0.0035 | +0.0001 | +0.0003 | +0.0004 | +0.0022 | +0.0003 | 1.8099 | 1.814(9) |
| $\omega_e$ | 598.4 | +3.1 | +2.4 | −0.1 | −0.8 | −1.3 | −2.2 | −0.2 | 599.2 | 575(25) |
| $D_e$ | 33.00 | +0.50 | −0.15 | −0.16 | −0.25 | −0.36 | +0.66 | +0.08 | 33.32 | 33.5(2) |
| $EA_e$ | 55.83 | +0.40 | −0.10 | −1.67 | −0.03 | −0.75 | +0.13 | +0.02 | 53.84 | 54.07(14) |
| | | | | | $IO^-$ | | | | | |
| $r_e$ | 1.9453 | −0.0034 | −0.0060 | +0.0012 | +0.0009 | +0.0001 | +0.0024 | +0.0004 | 1.9409 | 1.929(10) |
| $\omega_e$ | 593.5 | +2.7 | +0.4 | −0.7 | −0.5 | +0.2 | −2.6 | −0.4 | 592.5 | 581(25) |
| $D_e$ | 39.14 | +0.51 | −0.23 | −0.28 | −0.26 | −0.40 | +0.73 | +0.10 | 39.31 | − |
| $EA_e$ | 58.89 | +0.46 | −0.20 | −3.44 | −0.04 | −1.00 | +0.09 | +0.01 | 54.76 | 54.71(14) |

[a] See the footnotes to Table 2. The dissociation energies are given relative to $X^-(^1S_0) + O(^3P_2)$. The electron affinities refer to the ground electronic states of the neutral radicals. [b] Taken from refs 21, 23, and 24. Values in parentheses denote the stated experimental uncertainty in the last digit. The experimental $EA_e$ values were derived from the adiabatic $EA_0$s using the accurate *ab initio* (anharmonic) zero-point energies (in kcal/mol: 0.96 for $ClO^-$, 0.86 for $BrO^-$, 0.85 for $IO^-$, 1.22 for ClO, 1.04 for BrO, and 0.96 for IO). The experimental $D_e$ values were derived using the experimental molecular and atomic electron affinities (refs 21,24,71,72) and $D_0$(XO) values (ref 11 for ClO and ref 12 for BrO).

**TABLE 5: Summary of Calculated Dissociation Energies and Heats of Formation for the $X_1{}^2\Pi_{3/2}$ Ground States of ClO, BrO, and IO with Comparison to the Available Experimental Results (in kcal/mol)**

| | $D_0$ | | | $\Delta H_f$ (0 K) | | $\Delta H_f$ (298 K) | |
|---|---|---|---|---|---|---|---|
| | direct[a] | via $XO^-$[b] | expt | ab initio[c] | expt | ab initio[c] | expt |
| ClO | 63.4 | 63.5 ± 0.3 | 63.43 ± 0.01[11] | 24.1 ± 0.3 | 24.15 ± 0.03[11] | 24.2 ± 0.3 | 24.29 ± 0.03[11] |
| BrO | 55.7 | 55.8 ± 0.4 | 55.9 ± 0.1[12]<br>55.2 ± 0.4[13] | 31.4 ± 0.4 | 31.3 ± 0.1[12]<br>32.0 ± 0.4[13] | 29.6 ± 0.4 | 29.5 ± 0.1[12]<br>30.2 ± 0.4[13] |
| IO | 54.2 | 54.2 ± 0.6 | 53 ± 3,[74] 55 ± 2[73]<br>55.3 ± 0.5[d] | 30.4 ± 0.6 | 32 ± 3,[74] 30 ± 2[73]<br>29.3 ± 0.5[d] | 29.9 ± 0.6 | 31 ± 3,[74] 29 ± 2[73]<br>28.8 ± 0.5[d] |

[a] Derived from the ab initio results of Table 2. [b] Ab initio results utilizing the relation $D_0(XO) = D_0(XO^-) + EA(X) - EA(XO)$ with experimental electron affinities taken from refs 21, 23, 24, 71, and 72. [c] Calculated from the dissociation energies based on the negative ion cycles. See footnote b. The following reference thermodynamic data (ref 79) were utilized throughout (in kcal/mol): $\Delta H_f$ (O) = 58.98 ± 0.02 (0 K), 59.55 ± 0.02 (298 K); $\Delta H_f$ (Cl) = 28.590 ± 0.001 (0 K), 28.992 ± 0.002 (298 K); $\Delta H_f$ (Br) = 28.18 ± 0.01 (0 K), 26.74 ± 0.01 (298 K); $\Delta H_f$ (I) = 25.61 ± 0.01 (0 K), 25.52 ± 0.01 (298 K). [d] The experimental heat of formation derived in ref 75 (27.7 ± 1.2 kcal/mol at 298 K) from the kinetics of the IO + ClO reaction has been revised upwards by 1.1 kcal/mol with a concomitant decrease in its uncertainty by using a more recent experimental determination[76] of $\Delta H_f$ (OClO), 23.53 ± 0.24 kcal/mol at 298 K, and the $\Delta H_f$ (ClO) derived from ref 11.

second route leads to the most accurate dissociation energies in these cases because it minimizes errors due to spin−orbit effects, the two sets of $D_0$ values agree to within 0.1 kcal/mol in each case. The thermal corrections to the heats of formation at 0 K (to yield $\Delta H_f$ values at 298 K) have been determined using standard expressions for the ideal gas partition functions and experimental spectroscopic data where available.

Based on the spreads in the CBS extrapolation procedure and the experimental error bars in the electron affinities, best estimates of 63.5 ± 0.3, 55.8 ± 0.4, and 54.2 ± 0.6 kcal/mol have been determined for the $D_0$ values of ClO, BrO, and IO, respectively. The values for ClO and BrO clearly encompass the experimental values, however our predicted $D_0$ for BrO tends to favor the most recent experimental determination by North and co-workers,[12] although our error bars do not exclude the smaller value obtained by Wilmouth et al.[13] As in our previous work,[16] our final predicted $D_0$ for IO is in good agreement with the experimental crossed molecular beam measurements based on the O + ICl reaction,[73,74] although these latter values have rather large stated uncertainties. The top end of our predicted range also just overlaps with the lower end of the experimental error bars derived from the most recent kinetics experiments,[1,75] but only after updating their result with the most recent OClO dissociation energy.[76] This revision also significantly decreases the uncertainty in their experimental heat of formation and resulting dissociation energy. In addition, the presently predicted heat of formation for IO at 298 K, 29.9 ± 0.6 kcal/mol, can be compared to the values calculated previously by Hassanzadeh and Irikura,[77] 28.4 ± 1.8 kcal/mol, and McGrath and Rowland,[78] 30.5 ± 1.0 kcal/mol. Actually the level of agreement is remarkable given the very large differences in basis sets, correlation treatments, and methods for recovery of relativistic effects.

## IV. Conclusions

The spectroscopic and thermochemical properties of the halogen monoxides and their anions have been determined using high level electronic structure calculations that included explicit extrapolations to the complete basis set limit and full configuration interaction with additional corrections due to core−valence correlation and spin−orbit coupling. The resulting molecular constants exhibit excellent agreement with experiment for the neutral species and provide very reliable predictions for the anions. The final *ab initio* equilibrium bond lengths and harmonic frequencies for ClO and BrO differ from their accurate experimental values by an average of just 0.0005 Å and 0.8 $cm^{-1}$, respectively. The bond length of IO is overestimated by 0.0047 Å, presumably due to an underestimation of molecular spin−orbit coupling effects. The predicted bond lengths and harmonic frequencies for the closed-shell anions are expected to be accurate to within about 0.001 Å and 2 cm$^{-1}$, respectively. The dissociation energies of the radicals have been determined by both direct calculation and through use of negative ion thermochemical cycles, which made use of a small amount of accurate experimental data. The resulting values of $D_0$, 63.5, 55.8, and 54.2 kcal/mol for ClO, BrO, and IO, respectively, are the most accurate *ab initio* values to date, and those for ClO and BrO differ from their experimental values by just 0.1 kcal/mol. These dissociation energies lead to heats of formation, $\Delta H_f$ (298 K), of 24.2 ± 0.3, 29.6 ± 0.4, and 29.9 ± 0.6 kcal/mol for ClO, BrO, and IO, respectively. Also, the final calculated electron affinities are all within 0.2 kcal/mol of their experimental values. The inclusion of full iterative triple and quadruple excitations in the coupled cluster treatment was found to be critical for obtaining this high level of accuracy.

**Supporting Information Available:** The new iodine basis sets developed in this work, the additional core-valence functions added to the aug-cc-pVTZ-PP and aug-cc-pVQZ-PP basis sets for Br and I to yield aug-cc-pwCVTZ-PP and aug-cc-pwCVQZ-PP sets, and additional spectroscopic constants for the anions. This material is available free of charge via the Internet at http://pubs.acs.org. The iodine basis sets can also be downloaded in several formats from http://tyr0.chem.wsu.edu/∼kipeters/basissets/basis.html.

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