JOURNAL OF CHEMICAL PHYSICS VOLUME 113, NUMBER 24 22 DECEMBER 2000

The electronic structure and electron affinities of higher chlorine oxide radicals ClO_x $(x=2-4)$ from photoelectron spectroscopy of ClO_x^- anions

Xue-Bin Wang and Lai-Sheng Wang[a]
Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99352
and W. R. Wiley Environmental Molecular Sciences Laboratory, MS K8-88,
Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352

(Received 9 August 2000; accepted 26 September 2000)

The electronic structure of ClO_x $(x=2-4)$ radicals were experimentally investigated using anion photoelectron spectroscopy of the respective anions at several photon energies. The electron affinities of ClO_3 and ClO_4 were obtained for the first time and were found to be very high, 4.25 ± 0.10 and 5.25 ± 0.10 eV, respectively. Three low-lying excited states were observed for ClO_2 with excitation energies of 2.10 eV ($^2B_2$), $\sim$2.60 eV ($^2A_1$ and $^2A_2$). The $^2A_1$ and $^2A_2$ states were found to be nearly degenerate. Two low-lying states were observed for ClO_3 at $\sim$1.20 eV ($^2A_2$) and $\sim$2.65 eV (^2E), whereas no excited state was observed for ClO_4 even at our highest photon energy of 157 nm (7.866 eV). The photoelectron spectra were assigned and compared with available theoretical calculations. The excellent agreement between the experimental and theoretical results confirmed the previous calculations. © *2000 American Institute of Physics.*
[S0021-9606(00)00448-7]

I. INTRODUCTION

There has been considerable interest in the chemistry of chlorine-containing species since the discovery that chloroflurocarbons may play an important role in the stratospheric ozone depletion.[1] In the stratosphere, photodissociation of chloroflurocarbons releases a chlorine atom, which reacts with ozone ($Cl+O_3\rightarrow ClO+O_2$). In the mid-stratosphere, the chlorine mono-oxide molecule reacts with oxygen atoms ($ClO+O\rightarrow Cl+O_2$) to reform the chlorine atom, which can subsequently react with another ozone molecule. Despite the success of this commonly accepted mechanism, increasing recent evidence has shown that the higher chlorine oxides are also involved in the entire ozone depletion processes.[2–8] Therefore, it is highly desirable to understand the chemistry (formation and destruction) and structures (electronic and geometric) of the whole range of chlorine oxides in order to model and discover new channels for ozone depletion.

The photodissociation of ClO_2 has been extensively investigated.[9–11] It is generally known that after excitation by a near UV photon ($^2A_2\leftarrow X\,^2B_1$), the excited ClO_2 will dissociate, mainly to ClO+O. However, the second pathway ($ClO_2\rightarrow Cl+O_2$) may also be important. Interpretation of the observed dynamics needs to invoke two low-lying excited states ($^2B_2$ and $^2A_1$) that are expected to lie close to and interact strongly with the $^2A_2$ state.[10] These two states have not been observed in optical absorption experiments because the transition ($^2B_2\leftarrow X\,^2B_1$) is dipole-forbidden and the transition moment of $^2A_1\leftarrow X\,^2B_1$ is extremely weak.[12,13] Peterson and Werner[14–16] have performed multireference configuration interaction calculations of the low-lying electronic states of ClO_2. They calculated the term values and the geometric structures of ClO_2 for several low-lying excited states,[14] and discussed the roles of $^2B_2$ and $^2A_1$ in the photodissociation process.[15,16] Unlike optical absorption, which is subject to stringent selection rules, photoelectron spectroscopy (PES) of an anion can often access electronic states of the neutral molecules, that are optically ''dark,'' despite its relatively low resolution. Lineberger and coworkers[17] performed the first PES study on ClO^- and ClO_2^-, and obtained the electron affinity (EA) and vibrational frequencies of the ground state of ClO and ClO_2. They only observed the ground state of ClO_2, due to the low detachment photon energy used (351 nm–3.53 eV). Thus the predicted excited states ($^2B_2$ and $^2A_1$) remain unconfirmed experimentally.

For the higher chlorine oxides, there has been very little experimental and theoretical work on the chlorine trioxide (ClO_3) in spite of its relative importance. Francisco and co-workers[18,19] have very recently performed theoretical studies on the structure and low-lying excited states of ClO_3. There has been experimental evidence that the ClO_3 radical exists in aqueous solution and crystals.[20,21] The only experimental characterization of ClO_3 is from the study of Grothe and Willner, who reported IR and UV spectra of ClO_3 in a neon matrix.[22] The EA of ClO_3 was estimated to be >3.2 eV by Alekseev *et al.*[23] from the appearance potential for ClO_3^- following electron impact on perchloryl fluoride (ClO_3F). Recently, Beltran *et al.* studied a series of ClO_x^- $(x=1-4)$ and predicted an EA of 4.07 eV for ClO_3.[24]

Our knowledge about the ClO_4 radical is even less. Its existence in solid $KClO_4$ after irradiation remains controversial.[25] So far the only convincing experiment about ClO_4 is the isolation and IR characterization in a neon matrix by Grothe and Willner.[26] Huis and Schaefer[27] calculated the geometry and vibrational frequencies of the ground state of ClO_4, and predicted a very high EA. ClO_4 belongs to a class of molecules known as superhalogens[28–30] that possess

---

[a] Electronic mail: ls.wang@pnl.gov

higher EAs than the halogen atoms (the highest among all the atoms). The EA of ClO_4 was estimated to be 6.3 eV by Gutsev and Boldyrev.[28] But the recent and more accurate calculations by Huis and Schaefer yielded a lower value of 5.2 eV,[27] whereas Beltran *et al.* predicted a value of 5.1 eV.[24] Thus far, there has been no experimental measurement of the EA of ClO_4 and the theoretical predictions remain unconfirmed.

In the current work, we present a systematic PES study of the whole family of the higher chlorine oxide anions, ClO_x^- $(x=2-4)$ at several photon energies: 355 nm (3.496 eV), 266 nm (4.661 eV), 193 nm (6.424 eV), and 157 nm (7.866 eV). Our goal was to obtain information about the low-lying excited states and the EAs of the neutral ClO_x radicals and compare them with the available theoretical calculations. We showed that higher photon energies were necessary to study these species due to the high electron binding energies of the chlorine oxide anions. We observed that the EAs of ClO_x increase with the O content. Three excited states were observed for ClO_2, confirming the theoretical predictions of the $^2B_2$ and $^2A_1$ excited states. Two low-lying electronic excited states were also observed for the ClO_3 radical, whereas no excited state was observed for ClO_4 even at our highest photon energy used (157 nm).

II. EXPERIMENT

The experiments were carried out with an apparatus, which involves a magnetic-bottle time-of-flight photoelectron analyzer and an electrospray ion source. Details have been published elsewhere[31] and only a very brief description is given here. To produce the desired anions, we used a 10^{-4} molar solution of the corresponding salts ($NaClO_x$) at pH ~ 7 in a water/methanol mixed solvent (10/90 volume ratio). The solutions containing the ClO_x^- anions were sprayed through a 0.01 mm diameter syringe needle at -2.2 kV high voltage and under ambient atmosphere. Negatively charged molecular ions emerging from a desolvation capillary were guided by a radio frequency-only quadrupole ion guide into an ion trap, where the ions were accumulated for 0.1 second before being pushed into the extraction zone of a time-of-flight mass spectrometer.

In the PES experiment, the anions of interest were mass-selected and decelerated before being intercepted by a laser beam in the detachment zone of the magnetic-bottle photoelectron analyzer. Both a Nd:YAG laser (355 and 266 nm) and an excimer laser (193 and 157 nm) were used for photodetachment in the current investigation. The photoelectrons were collected at nearly 100% efficiency by the magnetic-bottle and analyzed in a 4-m long electron time-of-flight tube. The photoelectron time-of-flight spectra were then converted to kinetic energy spectra calibrated by the known spectra of I^- and O^-. The O^- anions were produced from photodissociation of ClO_2^- at 355 and 266 nm, as will be shown below. The binding energy spectra were obtained by subtracting the kinetic energy spectra from the corresponding photon energies. The energy resolution was about 11 meV (full width at half maximum) at 0.5 eV kinetic energy, as measured from the spectrum of I^- at 355 nm, and would deteriorate at higher kinetic energies.

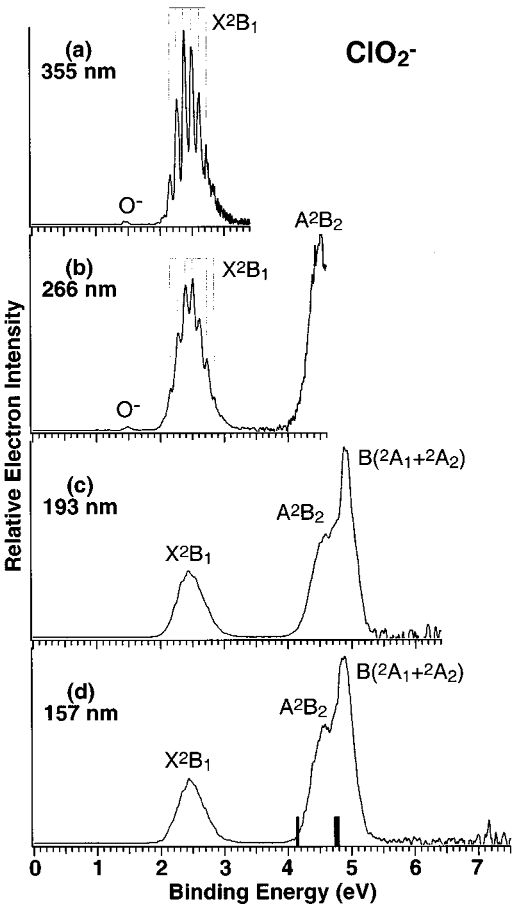

FIG. 1. Photoelectron spectra of ClO_2^- at (a) 355 nm (3.496 eV), (b) 266 nm (4.661 eV), (c) 193 nm (6.424 eV), and (d) 157 nm (7.866 eV). The vibrational structures in the 355- and 266-nm spectra are indicated. The theoretically predicted low-lying excited states for ClO_2 (Ref. 14) are indicated by the vertical bars in (d) (relative to the ground state).

III. RESULTS

The PES spectra of ClO_2^- are shown in Fig. 1 at four different photon energies. A well resolved vibrational progression was observed for the 355-nm spectrum of ClO_2^- [Fig. 1(a)], consistent with a much better resolved spectrum previously reported by Gilles *et al.*[17] The adiabatic electron binding energy (ADE) for ClO_2^- or the EA of ClO_2 was measured from the 0–0 transition to be 2.15 ± 0.03 eV. The vibrational frequency measured from the 355-nm spectrum of ClO_2^- was $910\pm80\ \mathrm{cm}^{-1}$, which is also consistent with the more accurate measurement reported previously $(945\pm25\ \mathrm{cm}^{-1})$.[17] This corresponds to the symmetric stretching frequency of ClO_2. Gilles *et al.* also resolved a bending mode $(445\pm25\ \mathrm{cm}^{-1})$, which was not resolved currently. The resolution of the spectrum shown in Fig. 1(a) was much poorer than the best resolution possible with our current apparatus due to a Doppler broadening as a result of the light mass of ClO_2^- and the difficulty to decelerate it before photodetachment. The 266-nm spectrum of ClO_2^- [Fig. 1(b)] revealed an additional feature (A) at a higher binding energy. The weak feature around 1.5 eV in the 355- and 266-nm

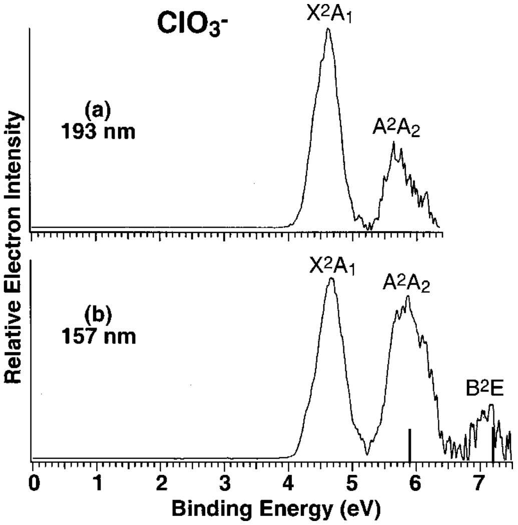

FIG. 2. Photoelectron spectra of ClO_3^- at (a) 193 nm and (b) 157 nm. The theoretically predicted vertical excitation energies (Ref. 19) for the neutral ClO_3 radical are indicated by the vertical bars in (b) (relative to the ground state).

TABLE I. Experimental adiabatic (ADE), vertical (VDE) detachment energies, and spectroscopic constants for the ground and low-lying excited states of ClO_x $(x=2-4)$, compared to the literature values.

	ADE (eV)		VDE (eV)	Term value (eV)	
	Current	Literature	Current	Current	Literature
ClO_2 $X\ ^2B_1$	2.15(0.03)[b]	2.140(8)[c]	2.38(0.05)	0	0
$A\ ^2B_2$	4.25(0.10)		4.55(0.10)	2.10(0.10)	1.98[e]
$B\ ^2A_1$	4.75(0.10)		4.90(0.10)	2.60(0.10)	2.60[e]
$C\ ^2A_2$[a]				(2.60)	2.62[e]
ClO_3 $X\ ^2A_1$	4.25(0.10)[b]		4.65(0.10)	0	0
$A\ ^2A_2$	5.45(0.10)		5.75(0.15)	1.20(0.10)	1.25[f]
$B\ ^2E$	6.9(0.1)		7.1(0.1)	2.65(0.10)	2.55[f]
ClO_4 $X\ ^2B_2$	5.25(0.10)[b]	5.19[d]	5.50(0.10)		

[a] Overlapped with the $B\ ^2A_1$ state (Fig. 1). Note that this state has been designated as "$A\ ^2A_2$" in all previous literature (Refs. 9–16).

[b] The measured adiabatic electron affinity.

[c] From Ref. 17.

[d] Theoretical value from Ref. 27. Reference 24 gives a theoretical value of 5.1 eV.

[e] Theoretical values from Ref. 14.

[f] Theoretical vertical excitation energies from Ref. 27.

spectra was due to O^-, as a result of photodissociation, $ClO_2^- \rightarrow ClO + O^-$, and the subsequent detachment of O^- by a second photon within the same laser pulse (~7 ns pulse width). At 193 nm [Fig. 1(c)], a more intense feature at ~5 eV (B) was also observed. However, the 157-nm spectrum [Fig. 1(d)] showed no more higher binding energy features.

The spectrum of ClO_3^-, measured at 193 and 157 nm, are shown in Fig. 2. Because of the anticipated high electron binding energies for ClO_4^-, we only measured its spectrum at 157 nm, as presented in Fig. 3. No vibrational structures were resolved in the spectra of ClO_3^- and ClO_4^-. Their ADEs were estimated by drawing a straight line at the leading edge of the ground state transition and then adding a constant to the intercept with the binding energy axis to take into account the instrumental resolution and a finite thermal effect. The ADEs so obtained for ClO_3^- and ClO_4^- were 4.25 ± 0.10 and 5.25 ± 0.10 eV, respectively, with relatively large uncertainties. Beside the ground state feature (X), the 193-nm spectrum of ClO_3^- [Fig. 2(a)] also showed a higher binding energy feature (A) at ~5.75 eV. At 157 nm [Fig. 2(b)], the intensity of the A feature was enhanced, in addition to a new and weak feature (B) at ~7.1 eV. For ClO_4^-, only one detachment transition was observed (Fig. 3) even at our highest photon energy available.

The obtained ADEs and vertical detachment energies (VDEs) for all the observed spectral features are given in Table I. All the VDEs were measured from the peak maxima. The ADEs of the higher binding energy transitions for ClO_2^- and ClO_3^- were estimated in the same manner as that for the ground state of ClO_3^- and ClO_4^-. The ADE for the B feature of ClO_2^- was a rough estimate because of its overlap with the A band.

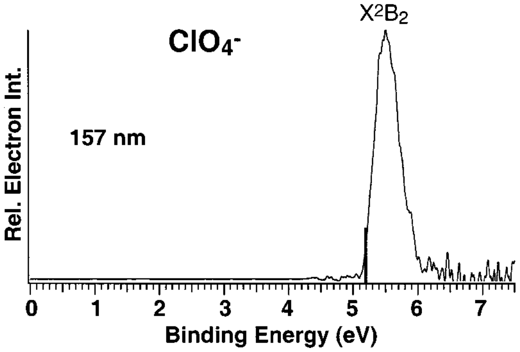

FIG. 3. Photoelectron spectrum of ClO_4^- at 157 nm. The calculated adiabatic electron affinity of ClO_4 is indicated by the vertical bar (Ref. 27).

IV. SPECTRAL ASSIGNMENTS AND DISCUSSION

A. ClO_2^- and ClO_2

The ClO_2^- anion is a closed shell molecule with C_{2v} symmetry. The bond length (Cl–O) and bond angle were measured in NH_4ClO_2 and $AgClO_2$ crystals, to be 1.57 Å and 110.5°.[32] The corresponding gas-phase values calculated by Peterson and Werner[33] are 1.583 Å and 113.7°. The ground state of ClO_2^- is $X\ ^1A_1$ with the following configuration: (innershell) $5b_2^2 8a_1^2 1a_2^2 3b_1^2$.[14]

The PES features in Fig. 1 represent transitions from the electronic ground state of the anion, ClO_2^-, to the ground and excited states of the neutral molecule, ClO_2. Under the single-electron approximation (Koopmans' theorem), the PES features can be viewed as removing electrons from the occupied molecular orbitals (MOs) from the anion. The final states of ClO_2 are then $^2B_1$, $^2A_2$, $^2A_1$, and $^2B_2$, upon removing one electron from the $3b_1$, $1a_2$, $8a_1$, and $5b_2$ orbitals, respectively. The exact ordering of these states was calculated previously to be $^2B_1 < ^2B_2 < ^2A_1 < ^2A_2$ in the direction of increasing energy. The ground state (X) of ClO_2 is then $^2B_1$. Among the first four low-lying states, the $^2A_1$ and $^2A_2$ states were calculated to be almost degenerate.[14] On the basis of these theoretical results, the assignments of the PES spectra of ClO_2^- were straightforward, as shown in Fig. 1 and

Table I. Apparently, the three excited state features were congested in the PES spectra (Fig. 1). In particular, the $^2A_1$ and $^2A_2$ states, assigned to the observed *B* band, nearly completely overlapped each other [Fig. 1(d)]. The calculated term values are 0.00, 1.98, 2.60, and 2.62 eV, respectively, and are compared with the current experimental values in Table I, as well as in Fig. 1(d) (relative to the adiabatic transition of the ground state). It is clear that the agreement between the theoretical and experimental results is excellent. Our 157-nm spectrum [Fig. 1(d)] also indicated that the detachment energy corresponding to the next excited state of ClO_2 is larger than ~ 7.9 eV (the 157 nm photon energy) because no more features were observed at the higher binding energy side of the 157-nm spectrum. This observation suggested that the next excited state of ClO_2 should occur at an excitation energy larger than 5.8 eV $(7.9-2.1)$. This estimate is consistent with the previous optical absorption spectrum,[34] which indicated that the next absorption started at 6.78 eV.

Several groups have calculated the bond length and bond angle of the ground state of the ClO_2 radical.[35,36] The most reliable one is from Peterson and Werner who obtained the following values: 1.476 Å for the Cl–O bond length and 117.9° for the Cl–O–Cl angle.[14] Gilles *et al.* performed a Franck–Condon analysis on their highly resolved ground state PES band of ClO_2^- and derived an anion Cl–O bond length (~ 0.1 Å longer than that of the neutral) and a bond angle (increased by $\sim 4°$ relative to that of the neutral).[17] Therefore, the vibrational progression of the X feature was dominated by the symmetric stretching mode. The frequency we obtained was 910 (80) cm^{-1}, compared to the 945 (25) obtained by Gilles *et al.*[17] and the more accurate value of $945.95\ cm^{-1}$ by Ortigoso *et al.*[37]

The first excited state of ClO_2 ($^2B_2$) was predicted to have almost the same bond length (1.597 Å), but a very sharp bond angle ($\sim$90°), relative to the anion structure (1.583 Å and 113.7°).[14] The frequency of the bending mode was expected to be small ($\sim 319\ cm^{-1}$). Our spectra (Fig. 1) exhibited a smooth band (*A*) with no resolved vibrational structure, consistent with the expected geometry changes. The optimized structures of the $^2A_1$ state (1.612 Å, 120.0°) and the $^2A_2$ state (1.631 Å, 106.4°)[14] are rather similar to that of the anion ground state. Therefore the *B* feature corresponding to these two states is relatively sharp. The current PES results provide a unique confirmation for the previous theoretical calculations on the ClO_2^- anion and the ClO_2 radical.

Finally, the observation of photodissociation of ClO_2^- at 355 and 266 nm [Figs. 1(a) and 1(b)] should be discussed. The fact that similar dissociation was not observed at 193 and 157 nm suggested that the dissociation probably involved a resonance absorption at 355 and 266 nm, which would correspond to quasi-bound states because they are above the detachment threshold. The photochemistry of the neutral ClO_2 radical has been well studied.[9–11] Similar photochemistry for the ClO_2^- anion is interesting, but not known. It should be pointed out that the dissociation of ClO_2^- could also produce $O+ClO^-$. The ClO^- product would be more difficult to detect in our experiment because of its broad Franck–Condon transitions and the fact that detachment transitions of ClO^- happen to overlap with that of the parent ClO_2^- and would be buried in the background.[17] The O^- dissociation channel of ClO_2^- at 355 and 266 nm provides us with a convenient atomic transition for our routine spectral calibration at the low binding energy range.

B. ClO_3^- and ClO_3

The chlorate anion (ClO_3^-) is a common anionic species in solution and solid. The symmetry of the ClO_3^- ground state is C_{3v}.[38] The Cl–O bond length and Cl–O–Cl bond angle were measured from crystals, ranging from 1.485 Å and 106.3° in $Ba(ClO_3)_2\cdot H_2O$ to 1.502 Å, 106.8° in $NaClO_3$.[39,40] The electronic configuration for the ground state of ClO_3^- (X^1A_1) is (innershell) $(4e)^4(1a_2)^2(4a_1)^2$.[19] The first three low-lying states of the ClO_3 radical are then $^2A_1$, $^2A_2$, and ^2E, upon removing one electron from the three highest occupied MOs, $4a_1$, $1a_2$, and 4e, of the anion, respectively. The three PES features in Fig. 2 were assigned according to these three states.

The vertical excitation energies for the first three excited states of ClO_3 have been recently calculated[19] and are compared to the current experimental results in Table I and Fig. 2(b). The first two excited states we observed are in excellent agreement with the calculated excitation energies. The third excited state was calculated to have a vertical excitation energy of 3.55 eV, which would correspond to a VDE of ~ 8.2 eV, just beyond the range of our 157-nm photon energy. The optimized bond length and bond angle of the ground state of the ClO_3 radical ($X\,^2A_1$) has been calculated to be 1.458 Å and 114.2°, respectively.[19,24] Compared to the anion structure (1.485 Å, 106.3°), the bond length of the radical slightly decreases by ~ 0.027 Å, but the bond angle increases by $\sim 8°$. Thus, the width of the first PES feature of ClO_3^- (Fig. 2) was most likely due to the low frequency bending mode. The structural parameters for the two excited states, $^2A_2$ and ^2E, are unknown. The vertical excitation energies of these two states were predicted to be 1.25 and 2.55 eV, respectively, at the ground state ($X\,^2A_1$) geometry.[19] The transition of $^2A_2 \leftarrow X\,^2A_1$ is dipole-forbidden and cannot be observed in optical absorption experiments. From the estimated ADEs of the three features in Fig. 2, we obtained the adiabatic excitation energies (term values) for the $^2A_2$ and ^2E excited states to be 1.20 ± 0.10 and 2.65 ± 0.10 eV, respectively.

Similarly, from the VDEs of the three features, the excitation energies of the $^2A_2$ and ^2E states of the neutral at the anion's geometry were estimated to be 1.10 ± 0.10, and 2.45 ± 0.10 eV, respectively (VDEs of the $^2A_2$ and ^2E states relative to that of the $X\,^2A_1$ state). These values are conceptually different from the vertical excitation energies from the $X\,^2A_1$ ground state to that of the $^2A_2$ and ^2E states, as theoretically calculated.[19] However, they should be close to each other if the geometry changes among the anion and the low-lying states of the neutral molecule is not too large. Indeed the term values obtained from the spectra are very close (within our experimental accuracy) to the calculated vertical excitation energies (Table I).[19] The calculated vertical excitation energies for the $^2A_2$ and ^2E states are also indicated in Fig. 2(b). The broad spectral width of the $A\,^2A_2$ state, however, indicated that there is probably a relatively large geometry change between this state of ClO_3 and the ground state of ClO_3^-. The $B\,^2E$ band was not well resolved experimentally due to its weak intensity and the fact that there were significant noises at the high binding energy side. This state should also exhibit a Jahn–Teller effect.

The only previous experimental knowledge about the EA of ClO_3 was that it was >3.2 eV.[23] The current measured value of 4.25 ± 0.10 eV thus represents the first direct experimental measurement of this key physical property for the ClO_3 radical, and confirmed the high EA value predicted recently by Beltran *et al.*[24]

C. ClO_4^- and ClO_4

Perchloride (ClO_4^-) is a strong oxidizing agent and a common inorganic anion in solution with tetrahedral symmetry.[41] The Cl–O bond length in the gas phase was predicted to be 1.450 Å.[27,42] The chlorine atom in ClO_4^- has a formal oxidation state of $+7$ and all the valence electrons of chlorine are paired with the four oxygen atoms. Thus the extra electron is shared equally by the four oxygen atoms, resulting in an extremely high electron binding energy or high EA for ClO_4.[28] Gutsev and Boldyrev[28] predicted a very high EA of 6.3 eV for ClO_4 and considered it as a superhalogen. Huis and Schaefer have performed an extensive theoretical study of ClO_4 and predicted[27] that the global minimum of ClO_4 has a C_{2v} structure with a $^2B_2$ ground state. They calculated a more accurate EA of 5.19 eV for ClO_4, which is in excellent agreement with our measured value of 5.25 ±0.10 eV. The 5.1 eV EA value calculated by Beltran *et al.*[24] is also in good agreement with the current experimental measurement. The calculated EA by Huis and Schaefer is indicated in Fig. 3. Indeed, the 5.25 eV EA for ClO_4 represents one of the highest EAs that we have measured directly using PES.[29,30,43–47] The PES spectrum of ClO_4^- (Fig. 1) only showed one band, representing the transition from the ground state of the anion to the neutral ClO_4 radical. This band was relatively sharp, indicating that there are probably only moderate geometry changes between the ground state of the anion and the neutral.

V. CONCLUSIONS

We report a systematic photoelectron spectroscopic study on ClO_x^- ($x=2-4$) at several photon energies. The electron affinities for ClO_3 and ClO_4 were obtained for the first time and were found to be very high, 4.25 (10) and 5.25 (10) eV, respectively. Three low-lying electronic states were observed for ClO_2, confirming previous theoretical calculations for the low-lying excited states for this important atmospheric species. Photodissociation of ClO_2^- ($\rightarrow ClO+O^-$) was also observed at 355 and 266 nm, but not at 193 and 157 nm. Two low-lying excited states were observed for ClO_3 and the observed excitation energies were in good agreement with recent theoretical calculations. No excited states were observed for ClO_4 even at our highest photon energy (7.866 eV). The current experiments provide a systematic set of data on the low-lying excited states and electron affinities for the three important higher chlorine oxide radicals and confirmed previous theoretical calculations.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Chemical Science Division. This work was performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory, operated for the DOE by Battelle. L.S.W. is an Alfred P. Sloan Foundation Research Fellow.

[1] M. J. Molina and F. S. Rowland, Nature (London) **249**, 810 (1974).

[2] C. R. Webster, R. D. May, D. W. Toohey *et al.*, Science **261**, 1130 (1993).

[3] S. P. Sander, R. R. Friedl, and Y. L. Yung, Science **245**, 1095 (1989).

[4] S. S. Prasad, Nature (London) **285**, 152 (1980).

[5] S. Parthiban, B. N. Raghunandan, and R. Sumathi, J. Geophys. Res. **102**, 12927 (1997).

[6] A. Rauk, E. Tschuikow-Roux, Y. Chen, M. P. McGrath, and L. Radom, J. Phys. Chem. **97**, 7947 (1993).

[7] M. Jansen, G. Schatte, K. M. Tobias, and H. Willner, Inorg. Chem. **27**, 1703 (1988).

[8] A. J. Colussi and M. A. Grela, J. Phys. Chem. **97**, 3775 (1993).

[9] H. F. Davis and Y. T. Lee, J. Phys. Chem. **96**, 5681 (1992).

[10] H. F. Davis and Y. T. Lee, J. Chem. Phys. **105**, 8142 (1996), and reference therein.

[11] (a) J. L. Gole, J. Phys. Chem. **84**, 1333 (1980); (b) J. X. Zhang and P. A. Aker, *ibid.* **98**, 765 (1994).

[12] (a) E. C. Richard and V. Vaida, J. Chem. Phys. **94**, 153 (1991); (b) **94**, 163 (1991).

[13] A. Wahner, G. S. Tyndall, and A. R. Ravishankara, J. Phys. Chem. **91**, 2734 (1987).

[14] K. A. Peterson and H. J. Werner, J. Chem. Phys. **96**, 8948 (1992).

[15] K. A. Peterson and H. J. Werner, J. Chem. Phys. **105**, 9823 (1996).

[16] K. A. Peterson, J. Chem. Phys. **109**, 8864 (1998).

[17] M. K. Gilles, M. L. Polak, and W. C. Lineberger, J. Chem. Phys. **96**, 8012 (1992).

[18] M. A. Workman and J. S. Francisco, Chem. Phys. Lett. **279**, 158 (1997).

[19] Y. Li and J. S. Francisco, J. Chem. Phys. **112**, 8866 (2000).

[20] Z. Zuo, Y. Katsumura, K. Ueda, and K. Ishigure, J. Chem. Soc., Faraday Trans. **93**, 533 (1997).

[21] B. G. Hegde, A. Rastogi, R. Damle, R. Chandramani, and S. V. Bhat, J. Phys.: Condens. Matter **9**, 3219 (1997).

[22] H. Grothe and H. Willner, Angew. Chem. Int. Ed. Engl. **33**, 1482 (1994).

[23] V. I. Alekseev, L. I. Fedorova, and A. V. Baluev, Izv. Akad. Nauk. SSR, Ser. Khi. **X**, 1084 (1983).

[24] A. Beltran, J. Andres, S. Noury, and B. Silvi, J. Phys. Chem. A **103**, 3078 (1999).

[25] (a) J. R. Morton, J. Chem. Phys. **45**, 1800 (1966); (b) J. R. Byberg and S. J. K. Jensen, *ibid.* **52**, 5902 (1970); (c) J. R. Byberg, J. Phys. Chem. **99**, 13392 (1995).

[26] H. Grothe and H. Willner, Angew. Chem. Int. Ed. Engl. **35**, 768 (1996).

[27] T. J. V. Huis and H. F. Schaefer III, J. Chem. Phys. **106**, 4028 (1997).

[28] G. L. Gutsev and A. I. Boldyrev, Chem. Phys. **56**, 277 (1981).

[29] X. B. Wang, C. F. Ding, L. S. Wang, A. I. Boldyrev, and J. Simons, J. Chem. Phys. **110**, 4763 (1999).

[30] X. B. Wang and L. S. Wang, Chem. Phys. Lett. **313**, 179 (1999).

[31] L. S. Wang, C. F. Ding, X. B. Wang, and S. E. Barlow, Rev. Sci. Instrum. **70**, 1957 (1999).

[32] (a) R. B. Gillespie, R. A. Sparks, and K. N. Trueblood, Acta Crystallogr. **12**, 867 (1959); (b) J. Cooper and R. E. Marsh, *ibid.* **14**, 202 (1961).

[33] K. A. Peterson and H. J. Werner, J. Chem. Phys. **99**, 302 (1993).
[34] R. Flesch, E. Rühl, K. Hottmann, and H. Baumgärtel, J. Phys. Chem. **97**, 837 (1993).
[35] J. S. Francisco and S. P. Sander, J. Chem. Phys. **99**, 2897 (1993).
[36] B. T. Luke, J. Mol. Struct.: THEOCHEM **332**, 283 (1995).
[37] J. Ortigoso and R. Escribano, J. Mol. Spectrosc. **148**, 346 (1991).
[38] A. D. Walsh, J. Chem. Soc. **X**, 2301 (1953).
[39] S. K. Sikka, S. N. Momin, H. Rajagopal, and R. Chidambaram, J. Chem. Phys. **48**, 1883 (1968).
[40] M. E. Burke-Laing and K. N. Trueblood, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **33**, 2698 (1977).
[41] H. H. Eysel, Spectrochim. Acta **44**, 991 (1988).
[42] F. Ramondo, L. Bencivenni, R. Caminiti, and C. Sadun, Chem. Phys. **151**, 179 (1991).
[43] H. Wu, X. Li, X. B. Wang, C. F. Ding, and L. S. Wang, J. Chem. Phys. **109**, 449 (1998).
[44] G. L. Gutsev, B. K. Rao, P. Jena, X. B. Wang, and L. S. Wang, Chem. Phys. Lett. **312**, 589 (1999).
[45] X. B. Wang, J. B. Nicholas, and L. S. Wang, J. Phys. Chem. A **104**, 504 (2000).
[46] X. B. Wang and L. S. Wang, J. Chem. Phys. **112**, 6959 (2000).
[47] X. B. Wang and L. S. Wang, J. Phys. Chem. A **104**, 4429 (2000).