Electronic structure of chromium oxides, CRo$_n^-$ and CRo$_n$ (n=1–5) from photoelectron spectroscopy and density functional theory calculations

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The electronic structure of CRo$_n^-$ and CRo$_n$ (n=1–5) was investigated using anion photoelectron spectroscopy and density functional theory. Photoelectron spectra of CRo$_n^-$ were obtained at several photon energies and yielded electron affinities, vibrational and electronic structure information about the neutral CRo$_n$ species. Density functional theory calculations were carried out for both the neutrals and anions and were used to interpret the experimental spectra. Several low-lying electronic states of CrO were observed and assigned from photodetachment of the CRo$^-$ ground state (6Σ$^-$) and an excited state (4II), which is only 0.1 eV higher. The main spectral features of CRo$_2^-$ were interpreted based on a $C_{2v}$ CRo$_2$ (4B$_1$). A very weak CRo(2$^+$) isomer was also observed with lower electron binding energies. Relatively simple and vibrationally resolved spectra were observed for CRo$_3^-$, which was determined to be $D_{3h}$. The CRo$_3$ neutral was calculated to be $C_{3v}$ with the Cr atom slightly out of the plane of the three O atoms. The spectrum of CRo$_5^-$ revealed a very high electron binding energy. Several isomers of CRo$_4^-$ were predicted and the ground state has a distorted tetrahedral structure ($C_2$) without any O–O bonding. Only one stable structure was predicted for CRo$_5$ with a superoxo O$_2$ bonded to a $C_{3v}$ CRo$_3$.

I. INTRODUCTION

Transition metal (TM) oxides are technologically important materials and have numerous applications, such as catalysts in conversion processes of hydrocarbons.$^{1,2}$ These materials exhibit different stoichiometries due to the existence of various oxidation states of the TM metals. Oxides of chromium, in particular, are widely used as coating materials in magnetic recording devices.$^{3,4}$ It was found that properties of these devices depend strongly on the stoichiometry of the chromium oxides. Investigations of the structural and electronic properties of TM oxide clusters with different metal to oxygen ratios help to understand the physical and chemical properties of the bulk materials and provide valuable insights into their perspective applications. In the present article, we report an investigation of the simplest chromium oxide species, CRo$_n^-$ and CRo$_n$ (n=1–5), using anion photoelectron spectroscopy (PES) and density functional theory (DFT) calculations.

Among the small CRo$_n$ species, chromium trioxide shows a very high electron affinity (EA), which indicates that it should be a strong oxidizing agent.$^5$ Species with large EAs have the ability to trap free electrons in excited gases and form extremely stable negative ions. Accurate EA values of the CRo$_n$ species can also be used for an improvement of thermodynamic data, but they have been difficult to obtain. For example, the EA values of CRo$_3$ deduced from previous thermodynamic methods vary widely from 3.16 to 4.05 eV.$^5$ On the other hand, PES, applied previously to many 3d TM oxide clusters in our laboratory and Lineberger’s group,$^7–19$ is based on direct measurements of the electron detachment energies and allows more precise EA determinations. Since PES of anions reflects transitions from anion states to the corresponding neutral states, it provides information on the electronic structure of both the anions and their neutral parents. In our recent study of MnO$_n^-$, we found that theoretical calculations are very helpful in the interpretation of the photoelectron spectra, as well as in understanding the electronic and geometrical structures of both the anions and the neutral species. A similar approach is applied here to the CRo$_n^-$ series, especially for n=3–5, for which there is little previous work.

Among the 3d TM oxide anions, theoretical studies have been performed for ScO$_2^-$, TiO$_2^-$, VO$_2^-$, MnO$_2^-$, FeO$_2^-$, and good agreement between experimental data and the calculated EA’s of the corresponding neutral species has generally been obtained. Detailed studies of the electronic and geometrical structure of the neutral and anionic 3d TM monoxides$^{20}$ and dioxides$^{20}$ have been performed using DFT methods with different generalized gradient approximations for the exchange-correlation functional. These studies showed that the BPW91 approach (an abbreviation for a combination of Becke’s exchange$^{21}$

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and Perdew–Wangs’ correlation\textsuperscript{32} functionals) provides similar results as the BLYP one (Becke’s exchange\textsuperscript{31} and Lee–Yang–Parr correlation\textsuperscript{33}), which are generally superior to those obtained by a hybrid Hartree–Fock–DFT B3LYP approach.\textsuperscript{34}

The current work is aimed at understanding the electronic and geometrical structures of the monochromic oxide species CrO\textsubscript{n} and CrO\textsubscript{n}\textsuperscript{−} (n = 1–5) using a combined experimental and theoretical study. Among these five oxide species, CrO\textsuperscript{2+} and CrO\textsuperscript{−} have been previously studied by PES at a lower photon energy.\textsuperscript{15,16} Several photon energies are used in the current work because higher photon energies are necessary for oxygen-rich species, which generally have very high EA’s. Geometrical structures for both the neutral and negatively charged clusters are optimized at the BPW91 level. Electron detachment energies were also calculated from anions and were used to help interpret the experimental PES data.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. Experimental method

Our experiments were performed with a magnetic bottle time-of-flight photoelectron spectrometer, which has been described in detail elsewhere.\textsuperscript{35,36} The apparatus is composed of a laser vaporization source, a time-of-flight mass spectrometer and a magnetic bottle time-of-flight electron analyzer. Chromium atoms, generated from laser vaporization of a pure Cr target, reacted with O\textsubscript{2} seeded in a helium carrier gas, producing a series of oxide clusters. The clusters entrained in the carrier gas underwent a supersonic expansion and collimated by a skimmer. Anions from the collimated beam were extracted perpendicularly into a time-of-flight mass analyzer. Desired anions were mass-selected and subsequently decelerated before crossing a detachment laser beam. Both a Q-switched Nd:YAG laser (532 nm–2.331 eV, 355 nm–3.496 eV, and 266 nm–4.661 eV) and an ArF excimer laser were used for photodetachment in the current experiments. The energy resolution of our apparatus was better than 30 meV for 1 eV electrons, as calibrated with Cu\textsuperscript{−}. Due to the dependence of the resolution on electron kinetic energies, lower photon energy spectra yielded better resolved data. But high photon energies were necessary to investigate species with high EA’s, as well as yielding more excited states of the neutral species.

B. Theoretical procedures

Our calculations were performed using an approach where linear combinations of atomic orbitals constitute one-electron molecular orbitals (MO-LCAO). The many-electron potential was constructed using DFT with a generalized gradient approximation for the exchange-correlation functional. A combination of Becke’s exchange\textsuperscript{31} and Perdew–Wangs’ correlation\textsuperscript{32} functionals, referred to as BPW91, was used as implemented in GAUSSIAN 94.\textsuperscript{37} For the atomic orbitals, we used the standard 6-311+G\textsuperscript{*} basis (Cr[15s11p4d1f/10s7p4d1f] and O[13s6p1d5s4p1d]) due to Wachters and Hay.\textsuperscript{38,39} Geometry optimizations were carried out by the steepest descent method until the gradient forces fell below the threshold value of 3 × 10\textsuperscript{−4} au. Analytical harmonic frequency calculations were performed subsequently to confirm that the optimized geometrical configurations corresponded to stationary states.

Density functional theory is valid for the lowest energy states in each particular (spatial and spin) symmetry.\textsuperscript{40–43} Extensive optimizations, beginning with different spatial configurations for each spin multiplicity for both the CrO\textsubscript{n} and CrO\textsubscript{n}\textsuperscript{−} series, were performed to ensure that the ground-state configurations were identified unambiguously. Comparison of the computed properties with experimental data was made to further verify our theoretical results. Vertical binding energies (E\textsubscript{b},\textsubscript{v}) or vertical detachment energies (VDE’s), which correspond to band maxima in photodetachment spectra, are due to a sudden detachment of an electron from an anion (A) to the corresponding neutral parent in some particular state N\textsubscript{j}. The quantity E\textsubscript{b},\textsubscript{v} can be evaluated at the equilibrium ground-state geometry R\textsubscript{A} of the anion as:

\[
E_{b,v} = E_{tot}(N, R_A) - E_{tot}(A, R_A).
\] (1)

With the present approach, only two transitions to neutral states N\textsubscript{j} (k = 1 and 2) can be computed directly. If the ground-state spin multiplicity of the anion is 2S + 1 = M, then we can compute the energies of electron detachment resulting in the two lowest neutral states with spin multiplicities 2S + 1 = M ± 1.

In order to evaluate transition energies to other neutral states, one could apply an approximate formula, which we used to assign features in the PES spectra of the MnO\textsubscript{n} anions:\textsuperscript{14}

\[
E_{b,j} = E_{tot}(N_{kn}, R_A) - E_{tot}(A, R_A) + (\varepsilon^A_{HOMO,n} - \varepsilon^A_{j,n}),
\] (2)

where k (1 or 2) denotes the neutral states accessible from the anion ground state as in Eq. (1), j > 2, n (a or β) denotes the spin representation, and \(\varepsilon^A_{j,n}\) are eigenvalues to the Kohn–Sham orbitals of the anion ground state, \(\varepsilon^A_{HOMO,n}\) is the eigenvalue to the highest occupied molecular orbital in the n spin representation.

Adiabatic detachment energies (A\textsubscript{ad}), corresponding to removal of an electron from the ground state of the anion to states of the neutral at their respective equilibrium geometries, are given by the differences in total energies of the neutral and anion states:

\[
A_{ad} = E_{tot}(N, R_N) + Z_N - E_{tot}(A, R_A) - Z_A = \Delta E_{el} + \Delta E_{mic},
\] (3)

where R\textsubscript{N} and R\textsubscript{A} denote ground-state equilibrium geometries of a neutral molecule (N) and its anion (A), respectively. Zero-point energies (Z) were computed within the harmonic approximation. While values of E\textsubscript{b},\textsubscript{v} correspond to band maxima in a PES spectrum, the A\textsubscript{ad} values are to be deduced from the thresholds of PES bands or the 0–0 transitions of vibrationally resolved bands. The A\textsubscript{ad} Value obtained for the ground-state transition corresponds to the EA of the neutral molecule. Electron affinity measures the total energy gain of a system due to attachment of an extra electron and represents an important thermodynamic quantity.
In order to estimate the thermodynamic stability of the chromium oxides, we also computed fragmentation energies as the differences in total energies of fragments $F_i$ formed in a particular decay channel and the total energy of an initial compound $M$:

$$D_x(M) = \sum_i E_{tot}(F_i) - E_{tot}(M),$$

where the zero-point energy corrections are neglected because they are relatively small.

III. EXPERIMENTAL AND THEORETICAL RESULTS

A. Experimental results

Figure 1 shows the spectra of CrO$^-$ measured at three photon energies. Well-resolved bands with vibrational structures were obtained. Many excited-state features were observed in the 266 nm spectrum [Fig. 1(c)], but they could not be clearly resolved and assigned beyond $\sim 3.5$ eV owing to limited resolution and spectral congestion. A high resolution spectrum of CrO$^-$ obtained at 351 nm was reported previously by Lineberger et al., but no detailed assignment was given. Generally, the current data agree well with the previous high resolution spectrum, with minor variations in relative intensities, due to the different experimental techniques employed (the current experiment is angle-integrated and measures electrons from all $4\pi$ solid angles). In particular, the 2.13 eV feature ($^5\Sigma$) is much stronger than the previous spectrum, whereas the 1.82 eV vibrational progression ($^5\Sigma^+ \rightarrow \Sigma^+$) appears to be weaker but with stronger hot band transitions (HB). Two more additional and relatively weak features could also be identified from the current spectra at 355 and 266 nm: the feature at 2.64 eV ($^1\Pi$) whose intensity was enhanced in the 266 nm spectrum and a vibrational progression starting at 3.03 eV ($^3\Delta$). More transitions were observed in the 266 nm spectrum, but they could not be definitely identified due to limited spectral resolution and congestion. The assignments were made on the basis of our theoretical calculations, as discussed later. The observed states are labeled in Fig. 1 (* indicates transitions from an excited anion) and compared with the theoretical calculations in Table 1. The observed detachment transitions and obtained spectroscopic constants are given in Fig. 2.

The spectra of CrO$_2^-$, shown in Fig. 3, were obtained at three detachment energies as well. The 355 nm spectrum [Fig. 3(a)] was vibrationally resolved with the 0–0 transition at 2.43 eV. There appears to be two vibrational progressions. The main progression has a vibrational spacing of about 900 cm$^{-1}$, and the other progression has a spacing of about 220 cm$^{-1}$. Very weak signals ($X^+ \rightarrow \Sigma^+$) were observed at $\sim 1.5$ eV. These signals completely disappeared when the carrier gas was seeded with N$_2$O, instead of O$_2$, as was the case for the 193 nm spectrum [Fig. 3(c)]. The weak features were likely due to a Cr(O$_2$)$^-$ isomer, as discussed later. The 266 nm spectrum [Fig. 3(b)] revealed two more intense features (A and B), compared to the 355 nm spectrum. The broadness of these features indicates that there must be significant geometry changes between the anions and the corresponding neutral states or there might be overlapping and unresolved electronic transitions. At 193 nm, there seemed to be unresolved features throughout the higher energy side beyond feature B. The relative intensities of the first three detachment bands in the 193 nm spectrum were changed compared to the 266 nm spectrum.

The weak low-binding energy feature around 1.5 eV completely disappeared in the 193 nm spectrum because an N$_2$O-seeded He carrier gas was used in this experiment. Similar behavior was observed in the 266 and 355 nm spectra taken under the same conditions. This feature is likely due to a peroxo species Cr(O$_2$)$^-$, which is consistent with the results of our previous DFT calculations performed for oxo, peroxo, and superperoxo isomers of chromium dioxide and its anion. The low EA of this isomer is also in agreement with a general anticipation that a 3d-metal oxygen peroxo complex M(O$_2$)$_2$ has a lower EA than the corresponding 3d-metal oxo complex OMO. A higher resolution spectrum of CrO$_2$ obtained at 351 nm was previously reported by Lineberger et al. However, the 351 nm photon energy allowed only the first detachment band to be observed. The current spectrum at 355 nm is consistent with the previous data, although the previous spectrum showed a much broader
Franck–Condon envelope for the X band, apparently due to intense hot band transitions.

Figure 4 shows the spectra of CrO$_3$ taken at two photon energies. The 266 nm spectrum [Fig. 4(a)] exhibited a well-resolved vibrational progression with an average spacing of 890 cm$^{-1}$. Two more well-separated and well-resolved bands (A and B) were observed in the 193 nm spectrum [Fig. 4(b)]. The weak features might be due to vibrational structures or possible overlapping transitions as revealed from our theoretical results. The weak feature a to the left of the A feature was due to a discrete detachment transition. As discussed later, several transitions might have contributed to the B feature.

Both CrO$_4$ and CrO$_5$ were found to have very high electron detachment energies and their spectra could only be observed at 193 nm, as shown in Fig. 5. Two well-resolved and intense features were observed for CrO$_4$ [Fig. 5(a)]. There were also weak features tailing the lower energy side

![Figure 2](image-url)  
**FIG. 2.** The observed detachment transitions from the two anionic states of CrO$^-$ and the spectroscopic constants of CrO.

![Figure 3](image-url)  
**FIG. 3.** Photoelectron spectra of CrO$_3$ at (a) 355 nm, (b) 266 nm, and (c) 193 nm (6.424 eV). The vertical lines in (a) indicate resolved vibrational progressions.

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**TABLE I. Experimental (Expt.) and calculated vertical electron detachment energies (eV) from the two lowest-lying states of CrO$^-$**

<table>
<thead>
<tr>
<th>Electron configuration</th>
<th>Final state BPW91 6-311+G*</th>
<th>BPW91 Augmen.*</th>
<th>BLYP 6-311+G*</th>
<th>BLYP Augmen.*</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrO$^-$ ($^6\Sigma^+$) 9σ$^1$ 1δ$^4$ 4π$^2$</td>
<td>5</td>
<td></td>
<td>1.22</td>
<td>1.24</td>
<td>1.06</td>
</tr>
<tr>
<td>CrO$^-$ ($^4\Pi$)$^*$ 9σ$^1$ 1δ$^4$ 4π$^2$</td>
<td>5</td>
<td></td>
<td>2.17</td>
<td>2.22</td>
<td>1.93</td>
</tr>
<tr>
<td>CrO$^-$ ($^2\Sigma^+$) 9σ$^1$ 1δ$^4$ 4π$^2$</td>
<td>5</td>
<td></td>
<td>2.47</td>
<td>2.41</td>
<td>2.23</td>
</tr>
<tr>
<td>CrO$^-$ ($^2\Sigma^+$) 9σ$^1$ 1δ$^4$ 4π$^2$</td>
<td>5</td>
<td></td>
<td>3.84</td>
<td>3.89</td>
<td>3.69</td>
</tr>
<tr>
<td>CrO$^-$ ($^2\Sigma^+$) 9σ$^1$ 1δ$^4$ 4π$^2$</td>
<td>5</td>
<td></td>
<td>4.99</td>
<td>4.91</td>
<td>4.62</td>
</tr>
</tbody>
</table>

$^a$Basis Cr[19s13p11d6f] is obtained by adding exponents intermediate between those of the standard 6-311+G* basis and five diffuse f functions. For O, the standard 6-311+G(3df) basis is used.

$^b$Energy in eV relative to the 6$^1$ state.

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of the $X$ band and between the $X$ and $A$ bands. The low-energy tail could be due to minor isomers presented in the anion beam. As shown later from our theoretical calculations, the weak features between the $X$ and $A$ bands were in fact due to direct detachment transitions. The spectrum of CrO$_5$ revealed a very broad band ($X$) at lower binding energies and two features ($A$ and $B$) at higher binding energies. Our experimental results for CrO$_n$ ($n=2–5$) are summarized in Table II and compared to our theoretical results, as discussed below.

### B. Theoretical results

Optimized ground-state geometries of CrO, CrO$_2$, CrO$_3$, and CrO$_5$ and their anions are presented in Fig. 6. Many low-lying isomers and excited states of CrO$_2$ and CrO$_3$ are found and are shown in Fig. 7. Theoretical investigations of CrO$_2$ with several isomers were reported in more detail previously, and Fig. 6 only displays the oxo ground state for CrO$_2$ ($^3B_1$) and CrO$_2$ ($^3B_1$). The structures of low-lying

### TABLE II. Observed vertical electron detachment energies (VDE) and spectroscopic constants for CrO$_n$ and CrO$_n^-$ ($n=2–5$) compared with theoretical results (Theor.) computed according to Eqs. (1) and (2).

<table>
<thead>
<tr>
<th>State</th>
<th>VDE (eV)</th>
<th>Vib. freq. (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt.</td>
<td>Theor.</td>
</tr>
<tr>
<td>CrO$_2$ $X^1B_2$</td>
<td>1.50(6)</td>
<td>1.37</td>
</tr>
<tr>
<td>CrO$_2$ $X^1B_1$, $^3B_1$</td>
<td>2.43(2)</td>
<td>2.35</td>
</tr>
<tr>
<td>CrO$_2$ $^5A_2^+$, $^3A_2^+$</td>
<td>4.25(5)</td>
<td>4.26</td>
</tr>
<tr>
<td>CrO$_2$ $^3A_1^+$, $^5B_1$, $^3B_1$</td>
<td>&gt;4.5</td>
<td>4.66</td>
</tr>
<tr>
<td>CrO$_3$ $X^1A^+$</td>
<td>3.66(2)</td>
<td>3.61</td>
</tr>
<tr>
<td>CrO$_3$ $a^1A^+_1$</td>
<td>4.61(2)</td>
<td>4.42</td>
</tr>
<tr>
<td>CrO$_3$ $^1A^+_1$, $^3A^+_1$</td>
<td>4.70(2)</td>
<td>4.61</td>
</tr>
<tr>
<td>CrO$_3$ $X^3A^+$, $^3A^+_2$</td>
<td>5.43(2)</td>
<td>5.57, 5.75</td>
</tr>
<tr>
<td>CrO$_4$ $X^1A^+$</td>
<td>5.07(4)</td>
<td>4.95</td>
</tr>
<tr>
<td>CrO$_4$ $a^1A^+$</td>
<td>6.04(3)</td>
<td>6.13</td>
</tr>
<tr>
<td>CrO$_5$ $X^3A^+$, $^3A^+_1$, $^5A^+_1$</td>
<td>4.69(2)</td>
<td>4.66, 4.70</td>
</tr>
</tbody>
</table>

The numbers in the parentheses represent uncertainties in the last digits.

Theoretical data for CrO$_2$ are from Ref. 30.

The symmetric stretching mode ($v_1$).

The bending mode ($v_2$).

Final states are labeled according to the $D_{3h}$ point group of the CrO$_n^-$ anion.
peroxo and superoxo isomers of CrO$_2$ and CrO$_2$ are not shown. In the current theoretical work, we focus on the monoxide and the higher oxides starting with CrO$_3$.

The ground state of CrO$_3$ ($^1A_1$) is closed shell with C$_{3v}$ symmetry and an out-of-plane angle of 15.6° (Fig. 6). Previous calculations using a local-spin-density-approximation (LSDA) approach and the LSDA with nonlocal corrections (NLSDA)\textsuperscript{44} yielded similar geometric structures with the Cr–O bond length being 1.59 and 1.62 Å at the LSDA and NLSDA levels, respectively. Our computed harmonic frequency for the symmetric stretching mode ($\omega$) of 959.6 cm$^{-1}$ is in good agreement with the value of 890 cm$^{-1}$ measured from the PES spectrum of CrO$_3$ (Table II). A value of 968.4 cm$^{-1}$ was obtained for this mode by Andrews et al.\textsuperscript{45} from infrared spectra of CrO$_3$ trapped in inert matrices. The lowest-energy isomers of CrO$_3$ were found to be well-separated in total energy from the ground state of CrO$_3$. The ground state (3$^2$A$^1$) of CrO$_3$ was separated in total energy from the ground state: a triplet oxo isomer of CrO$_3$ was found to be above the ground state by 1.04 and 2.27 eV, respectively.

An extensive search for a thermodynamically stable state of CrO$_3$ resulted in only one configuration ($^3A'$) of the superperoxo type, as shown in Fig. 6. The ground state ($^2A'$) of the CrO$_3$ anion has the same superoxo shape and is below the ground state of the neutral parent by 4.41 eV. We found another isomer for CrO$_3$, which also has a doublet spin multiplicity with a double peroxo geometrical shape. This isomer is above the ground state anion by 1.81 eV.

### IV. DISCUSSION AND COMPARISONS OF EXPERIMENTAL AND THEORETICAL RESULTS

#### A. CrO and CrO$^-$

The ground state of CrO is known to be 5$^2$II with an electron configuration, 1s$^2$2p$^1$3s$^1$.\textsuperscript{46,47} Upon formation of the anion, the extra electron can enter either the 9s$^1$MO to give a 4$^2$II state or the 4p$^1$MO to give a 6$^2$' state. Our theoretical results, as given in Table I, suggest that the two states are nearly degenerate in total energy. Direct computations of VDE’s from the two anions to the neutral CrO states were performed according to Eq. (1) and VDE’s to excited states of CrO were computed according to Eq. (2). Our results obtained at the BWPW91 and BLYP levels of theory with the use of two basis sets (the 6-311+G$^*$ basis and an augmented 6-311+G$^*$ one), are given in Table I. The variations at the different levels of theory are rather small and the ordering of the energy levels obtained is consistent.

The strong peak at 1.22 eV is assigned to be the transition from the ground state of the anion to the ground state of the neutral. This assignment is consistent with that of Lineberger et al.\textsuperscript{15} The obtained EA is also in excellent agreement with the previous value of 1.221 eV. The peaks at lower binding energies appeared as hot band transitions. However, as was pointed out previously by Lineberger et al.,\textsuperscript{15} the peak at 1.12 eV is too intense to be due to a hot band transition. It was assigned to be from an excited state of the anion. Comparing the current spectra to that of Lineberger et al., we note that the excited anion state was even more populated in the current experiment. The observation of excited anions was consistent with our theoretical results, which indicated that there are two nearly degenerate anion states depending on which orbitals the extra electron enters. Experimentally, the two anionic states differ by 0.096 eV, according to the above assignment. Such a small energy difference could not be definitively distinguished at the current levels of theory, as one can see from Table I. Lineberger

![Figure 7](downloaded_from_7940_jchemphys.org_115_17_1_november_2001_gutsevet_al.png)
et al. assumed that the ground state of CrO\(^{-}\) was \(4\Pi\), but did not provide any spectral assignments.

The two strongest excited-state transitions correspond to the feature at 2.13 eV and the vibrational progression starting at 2.28 eV. The binding energies of these two states are in good agreement with the computed vertical binding energies for the \(5\Delta\) and \(5\Sigma^{+}\) states from the \(6\Sigma^{+}\) anion, respectively, as shown in Table I. The features observed at 1.82, 2.64, and 3.03 eV are in good agreement with the three low-lying states derived from the \(4\Pi\) state of the anion (Table I). The weak intensities of these transitions suggested that they are more likely to be from the excited anion. Thus, the combined experimental and theoretical results allowed us to conclude that the \(6\Sigma^{+}\) state should be the ground state of the anion. Figure 2 shows the spectroscopic transitions and the obtained spectroscopic constants. The more accurate vibrational frequencies for the corresponding transitions observed by Lineberger et al. are also given in Fig. 2.

The vibrational frequency \((\omega_{v})\) of CrO computed\(^{29}\) at various levels of theory is 911 cm\(^{-1}\) (BPW91), 903 cm\(^{-1}\) (BLYP), and 870 cm\(^{-1}\) (B3LYP), which are all in good agreement with the average vibrational spacing of 920 cm\(^{-1}\) obtained from the present spectra, as well as with the previous more accurate gas-phase experimental value\(^{46}\) of 898 cm\(^{-1}\). Theoretical frequencies\(^{29}\) were also computed for the two anionic states: 827 cm\(^{-1}\) (BPW91), 810 cm\(^{-1}\) (BLYP), and 815 cm\(^{-1}\) (B3LYP) for \(6\Sigma^{-}\) and 879 cm\(^{-1}\) (BPW91), 876 cm\(^{-1}\) (B3LYP) for \(4\Pi\). The latter are also in reasonable agreement with the experimental value of 780±80 cm\(^{-1}\).

B. CrO\(_{2}\) and CrO\(_{2}^{-}\)

The ground state of CrO\(_{2}\) has a \(C_{2v}\) structure and a quartet electronic state \((^3B_{1})\) with an electronic configuration, \(9a_{1}^{2}3b_{2}^{2}6b_{2}^{1}10a_{1}^{2}4b_{1}^{1}11a_{1}^{1}\). Detachment of the electron from the \(11a_{1}\) HOMO leads to neutral CrO\(_{2}\) in its ground state \((^3B_{1})\) with an electronic configuration, \(9a_{1}^{2}3b_{2}^{2}6b_{2}^{1}10a_{1}^{2}4b_{1}^{1}\). The VDE corresponding to this process computed according to Eq. (1) is 2.35 eV, which is in good agreement with the first PES feature (X) of CrO\(_{2}\) at 2.43 eV (Fig. 3, Table II). Although both the ground states of CrO\(_{2}\) and CrO\(_{2}^{-}\} have \(C_{2v}\) symmetry, the neutral has a shorter Cr–O bond length and smaller \(\angle\)–Cr–O angle, as shown in Fig. 6. These geometry changes between the anion and the neutral are consistent with the PES spectra [Fig. 3(a)], which revealed vibrational excitations in two modes. The 900 cm\(^{-1}\) mode should be due to the Cr–O symmetric stretching and the 220 cm\(^{-1}\) mode the bending mode. These vibrational frequencies and assignments are consistent with those by Lineberger et al.\(^{16}\)

The second direct computation of the detachment energy corresponds to removal of an electron from the \(6b_{2}^{2}\) MO [the topmost MO in the \(\beta\) (minority) spin representation] and yielded a VDE of 4.26 eV, which corresponds to the vertical detachment to a \(^3A_{2}\) final neutral state. This computed VDE value is in excellent agreement with the VDE of the B band (4.25 eV) in the PES spectra (Fig. 3). Applying Eq. (2), we estimated approximate detachment energies from other valent MOs as given in Table II. It was found that the VDE’s for detachment from the \(4b_{1}(^3A_{1})\) and \(10a_{1}(^3B_{1})\) orbitals are very close (−2.73 eV) and they were assigned to correspond to the broad feature A observed around 3.4 eV. The 193 nm spectrum showed almost continuous signals above feature B, consistent with the presence of many closely spaced transitions due to detachments of electrons from the inner valent orbitals.

C. CrO\(_{3}\) and CrO\(_{3}^{-}\)

The ground state of neutral CrO\(_{3}\) has \(C_{3v}\) symmetry (Fig. 6) with a closed-shell electronic configuration, \(9a_{1}^{7}e^{4}1a_{2}^{5}(10a_{1})^{0}\) corresponding to a \(^1A_{1}\) state, whereas the CrO\(_{3}^{-}\) anion has \(D_{3h}\) symmetry and an electronic configuration \((1e)^{4}(3a_{2}^{3})^{4}(6e)^{4}(1a_{2}^{2})^{2}(7a_{1}^{1})^{1}\) which corresponds to a \(^2A_{1}\) state. Direct computations of detachment energies according to Eq. (1) to the singlet and triplet states provide values of 3.61 and 4.61 eV, respectively, in excellent agreement with the first two PES features at 3.66 eV (X) and 4.70 eV (A) (Fig. 4). The triplet neutral state (at the equilibrium anion geometry) has the electronic configuration \(\ldots (1a_{2}^{2})(7a_{1}^{1})\), which could be identified as corresponding to a \(^3A_{2}\) state of the neutral after the geometry relaxation takes place. The latter state is the lowest in total energy among the optimized triplet states of neutral CrO\(_{3}\) and is above the ground \(^1A_{1}\) state by 1.22 eV. The large vibrational progression observed for the X band indicates that there is a large geometry change between the ground states of the anion and the neutral. The 890 cm\(^{-1}\) vibrational spacing is in reasonable agreement with the calculated symmetric stretching frequency of 959.6 cm\(^{-1}\). The bond length change between the anion and the neutral ground state (Fig. 6) is also consistent with the observed vibrational progression. The change from \(D_{3h}\) CrO\(_{3}\) to \(C_{3v}\) CrO\(_{3}^{-}\) suggests that the out-of-plane bending mode should also be active in the X band. However, our calculations gave a very low bending frequency (43 cm\(^{-1}\)), which is too small to be resolved under our current experimental conditions.

Using Eq. (2) with two reference energies \([E_{\text{tot}}(A,1A_{1}^{1})-E_{\text{tot}}(A,2A_{1}^{1})]=3.61\) eV and \([E_{\text{tot}}(A,3A_{1}^{1})-E_{\text{tot}}(A,2A_{1}^{1})]=4.61\) eV, we obtained a set of energies corresponding to detachment of an electron with subsequent formation of singlet and triplet states: 4.42 eV \((^3A_{2}^{1})\), 5.18 eV \((^3E')\), 5.57 eV \((^3A_{2}^{0})\), 5.33 eV \((^3E')\), and 5.75 eV \((^3A_{2}^{0})\). Such closely spaced energies are related to the nearly same orbital energies in both majority and minority spin representations. The 4.42 eV transition \((^3A_{2}^{1})\) may correspond to the feature labeled \(a\) at 4.61 eV [Fig. 4(b)]. The third main detachment feature labeled \(B\) may then be due to detachment from the \(6e'^{1}\) and \(3a_{2}^{0}\) orbitals, corresponding to the last four calculated detachment transitions. The large intensity of feature B is consistent with the overlapping nature of the assigned transitions. The detachment from the \(1e'^{1}\) MO was computed to occur at 6.68 eV, which is beyond the 193 nm photon energy, consistent with our PES spectra. However, all the latter assignments can only be viewed as tentative. With our current one-electron approach, it is difficult to reach a quantitative assignment. Multireference theoretical models would be re-
quired to pin down the excited states of the CrO₃ neutral species. The seeming simplicity of the CrO₃ PES spectra may in fact contain complicated and overlapping detachment transitions.

D. CrO₄ and CrO₅

The ground state of CrO₄ is ¹A (C₂ symmetry) and its electronic configuration is 15a²13b². But there are two low-lying triplet states, as shown in Fig. 7. The triplet peroxo state is only 0.12 eV above the ground state CrO₄. The anion ground state has an electronic configuration of 13a²2a²7b²7b¹, corresponding to a ¹B₁ (C₂ᵥ) state, which is degenerate in total energy with a ²B₂ state. Detachment from the 7b₁ MO results in the neutral ¹A₁ ground state with [Eₜot(A,¹A₁) − Eₜot(A,²B₁)] = 6.13 eV, whereas detachment from 7b₂ leads to a ³A₂ state with [Eₜot(A,³A₂) − Eₜot(A,²B₁)] = 4.95 eV, which is slightly above the peroxo ³A₂ state, the lowest triplet state of the neutral (Fig. 7). These two detachment channels are in excellent agreement with the two main PES features at 5.07 eV (X) and 6.04 eV (A). Here, we met the case where the first vertical detachment of an extra electron from the singly occupied MO results in the formation of a neutral at C₂ᵥ symmetry, which would relax to C₃ᵥ symmetry. This is a really unusual situation: this first transition to the singlet ¹A state has an energy higher by 1.2 eV than the transition to the triplet ³A₂ state, which is higher in total energy but has a similar geometry as the anion. This suggests that the A band corresponding to removal of the 7b₁ electron should have a low-long energy tail extending to the left of the X band, not inconsistent with our PES spectrum [Fig. 5(a)]. Using Eq. (2) with two reference energies, we estimated energies of several other vertical transitions. The estimated singlet states are: 5.29 eV (¹A₂), 5.60 eV (¹B₂), 6.53 eV (¹A₂), and 6.71 eV (¹B₁); and the triplet states are: 5.03 eV (³B₂), 6.06 eV (³B₁), and 6.09 eV (³A₂). All these transitions except the 6.53 and 6.71 eV singlet states may be contained in the PES spectrum of CrO₄ [Fig. 5(a)].

E. CrO₅ and CrO₆

We found CrO₅ to possess only one thermodynamically stable state of a superoxo type (C₃v) with a triplet state ³A" [(8a")²(2a")²(9a")²(23a")¹(10a")¹]. The ground state of the CrO₅ anion is ³A" [⋯(23a")²(10a")¹] and has a similar C₃ᵥ geometrical shape as its neutral parent, as shown in Fig. 6. According to Eq. (1), detachment of an electron from the 23a" orbital results in the ³A" neutral ground state with a VDE of 4.69 eV, whereas detachment from the 10a" orbital reaches a dissociative ¹A' neutral state with a VDE of 5.17 eV. These two computed detachment channels are in good agreement with the broad band X, which should be due to two overlapping features. The broad nature of this band is consistent with the geometry changes between the anion and neutral ground state and the dissociative nature of the ¹A' state.

Using Eq. (2) with the two reference energies [Eₜot(A,³A") − Eₜot(A,²A")]+ = 4.69 eV and [Eₜot(A,¹A') − Eₜot(A,²A")]= 5.17 eV, we estimated VDE’s from other valence MO’s: 23a' (¹A')−5.60 eV, 9a" (³A")−5.45 eV, 9a" (³A")−5.66 eV, 22a' (³A")−6.21 eV, 22a' (³A")−6.37 eV, 8a" (³A")−6.21 eV, 8a" (³A")−6.45 eV. The 5.45 eV detachment energy from the 9a" orbital is in excellent agreement with the A band at 5.33 eV. The 22a' orbital is in excellent agreement with the B band at 6.08 eV. The large number of transitions closely spaced in energy is consistent with the complicated PES spectrum observed for CrO₆⁻.

F. Adiabatic electron affinities

The experimental and theoretical adiabatic electron affinities of the chromium oxides are summarized in Table III. The theoretical EA’s computed according to Eq. (3) are: 1.17 eV (CrO₄), 2.22 eV (CrO₃), 3.38 eV (CrO₃), 4.61 eV (CrO₃), and 4.41 eV (CrO₃). These computational data are in good agreement with the experimental values. The EA’s increase with the number of O atoms and saturate at CrO₄.

This trend is consistent with our previous observations of other oxide species and indicates a sequential oxidation of the Cr atom. Both CrO₄ and CrO₆ possess rather large EA’s for the 3d TM oxides was first proposed on the basis of calculations by an Xα-method. Our recent calculations of FeO₄ and FeO₃ by the BPW91 method confirmed that the reason is in the structure of the topmost MO, which accepts the extra electron. This MO is almost entirely composed of oxygen AO’s and is bonding with respect to oxygens. Note that the classical superhalogen MnO₄⁻ has the A₉D of 4.96 eV computed at the BPW91/6-311+G* level of theory, in good agreement with the experimental value of 4.8 eV obtained from the PES spectra of MnO₄⁻. The topmost MO of MnO₄⁻ is a pure oxygen one as is required by the superhalogen theory.

G. Fragmentation patterns

Table IV reports the fragmentation energies of CrO₃⁻ and CrO₄ computed according to Eq. (4). Experimental data are available for CrO and CrO₃⁻ and they are in fair agree-
ment with our computational results. Since Cr has a $4s^13d^5$ electronic configuration, it has a formal valence of six. However, the Cr–O bond is stronger in CrO$_2$ than that in CrO$_3$ in contrast to the anticipation based on the notion of maximum saturation of formal vacancies. CrO$_4$ is stable by about 55 kcal/mol while CrO$_3$ is stable by only 10 kcal/mol toward evolution of molecular oxygen.

The low-energy decay channels of CrO$_4^-$ anion correspond to detachment of an extra electron for $n = 1$–3. CrO$_5$ is almost equally stable toward detachment of an extra electron or dissociation of atomic and molecular oxygen. While CrO$_3$ is rather stable towards detachment of an extra electron and dissociation of an atomic oxygen, it is much less stable toward evolution of molecular oxygen, as would be expected due to the superoxo O$_2$ bonding in CrO$_5^-$. 

**V. SUMMARY**

We report a comprehensive theoretical and experimental investigation of CrO$_n^- (n = 1–5)$ and their corresponding neutral species. Photodetachment photoelectron spectra were obtained for the anions produced from a laser vaporization cluster source at various photon energies. Calculated adiabatic and vertical binding energies of CrO$_n$ are in good agreement with the experimental values. We show that theoretical calculations are very helpful in interpretations of the photoelectron spectra of the anions, in understanding the electronic and geometrical structures of their ground and excited states, and chemical bonding for both the anions and the neutral species.

**ACKNOWLEDGMENTS**

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sored by Department of Energy’s Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for the U.S. Department of Energy by Battelle.

**TABLE IV.** Fragmentation energies ($D_n$ in eV) of CrO$_n$ and CrO$_n^-$, computed according to Eq. (4).

<table>
<thead>
<tr>
<th>Channel</th>
<th>CrO$_n$ De</th>
<th>Channel</th>
<th>CrO$_n^-$ De</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrO→Cr+O</td>
<td>4.94</td>
<td>CrO$^-$→CrO$^+$ + e</td>
<td>1.17</td>
</tr>
<tr>
<td>CrO$_2$→Cr+O$_2$</td>
<td>5.11</td>
<td>CrO$_2^-$→CrO$_2^+$ + e</td>
<td>2.22</td>
</tr>
<tr>
<td>CrO$_3$→Cr+O$_3$</td>
<td>5.98</td>
<td>CrO$_3^-$→CrO$_3^+$ + e</td>
<td>6.11</td>
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<tr>
<td>CrO$_4$→Cr+O$_4$</td>
<td>5.48</td>
<td>CrO$_4^-$→CrO$_4^+$ + e</td>
<td>3.35</td>
</tr>
<tr>
<td>CrO$_5$→Cr+O$_5$</td>
<td>5.31</td>
<td>CrO$_5^-$→CrO$_5^+$ + e</td>
<td>4.64</td>
</tr>
</tbody>
</table>

$^a$Experimental $D_0$ value is $4.78\pm0.09$, see Ref. 51.

$^b$Experimental $D_0$ value is $5.47\pm0.05$, see Ref. 52.


$^{aq}$M. J. Frisch, G. W. Trucks, H. P. Schlegel et al., *Gaussian 94*, Revision B.1, Pittsburgh, PA.


$^{aw}$A. Gorling, S. B. Trickey, P. Gisdakis, and N. Rosh, *Topics in Organome-
