

A new interpretation of the CrO^- photoelectron detachment experiment

Charles W. Bauschlicher, Jr.*

Mail Stop 230-3

Space Technology Division

NASA Ames Research Center

Moffett Field, CA 94035

G. L. Gutsev†

Department of Chemistry

University of Virginia

Charlottesville, Virginia 22901

Abstract

CASSCF/MRCI calculations are performed on CrO^- and CrO . The ground state of CrO^- is identified as $^4\Pi$, not $^6\Sigma^+$, as recently suggested. We assign the experimental detachment features to the seven one-electron processes arising from the two ion states.

I. INTRODUCTION

Lineberger and co-workers¹ studied CrO^- using photoelectron spectroscopy. They suggested that the ground state of CrO^- is $^4\Pi$. They observed four neutral states,

*bauschli@pegasus.arc.nasa.gov

†Mailing address: Mail Stop 230-3, NASA Ames Research Center, Moffett Field, CA 94035

they assigned two of the states as $^5\Pi$ and $^3\Pi$, and suggested that one of the two other states might be $^5\Sigma^+$. They also observed an excited state of CrO^- only $750\pm 80\text{ cm}^{-1}$ above the ground state, which they suggested was the $^4\Phi$ state.!

OK

Very recently Wang and co-workers² studied CrO^- using photoelectron spectroscopy and density functional theory (DFT). They assigned the ground state of CrO^- as $^6\Sigma^+$ and the low-lying excited state as $^4\Pi$. They observed more neutral states than Lineberger and co-workers. While Wang and co-workers agreed with the previous assignment of the $^5\Pi$ state, they assigned the other two states differently. In addition, the Wang assignment differs with $^5\Sigma^+ - ^5\Pi$ and $^5\Delta - ^5\Pi$ excitation energies from optical spectroscopy^{3,4}.

We have recently observed that DFT can have problems with the relative separations between Σ and Π states for some transition metal compounds. In addition, the Wang assignment of the neutral states is based on DFT orbital energies, which is qualitative at best. Therefore we have undertaken high level calculations on CrO and CrO^- using the complete-active-space self-consistent-field/multireference configuration interaction (CASSCF/MRCI) approach. This level of theory can treat all of the states of interest, thereby avoiding the use of orbital energies to compute the energy separations.

II. METHODS

We perform internally contracted^{5,6} multireference configuration interaction (IC-MRCI) calculations. The effect of higher excitations is estimated using the multireference analog of the Davidson correction, and is denoted IC-MRCI+Q. The orbitals are determined using the complete-active-space self-consistent-field (CASSCF) approach. Excluding the $^4\Pi$ state of CrO^- , the Cr 3d and 4s orbitals and the oxygen 2p orbitals are in the active space. For the $^4\Pi$ state, one σ orbital is moved from the active to the inactive space since its occupation was essentially 2.0. To make the MRCI

calculations as equivalent as possible, this σ orbital is included in the active space in the MRCI calculations. In addition to the active orbitals, the oxygen 2s orbital is also correlated in the IC-MRCI treatment. However, only the CASSCF configurations are used as references; that is, the oxygen 2s orbital is in the inactive space. Finally we note that for the ${}^3\Phi$ state, a state-averaged calculation are performed which included the ${}^3\Pi$ and ${}^3\Phi$ states.

We use the Cr (20s15p10d6f4g)/[7s6p4d3f2g] averaged atomic natural orbital⁷ and oxygen augmented correlation-consistent polarized valence triple zeta (aug-cc-pVTZ) set^{8,9}. The calculations are performed using Molpro¹⁰.

III. RESULTS AND DISCUSSION

Our computed results for CrO and CrO⁻ are summarized in Table I along with experiment¹⁻⁴. We first compare our CrO results with those obtained by optical spectroscopy. For the ${}^5\Pi$ and ${}^5\Sigma^+$ states, the computed r_e and ω_e values are in good agreement with experiment⁴. The computed T_e for the ${}^5\Sigma^+$ state is about 1200 cm⁻¹ too small. The ${}^5\Sigma^-$ T_e actually agrees better with the experimental value, but the computed ω_e values show that the ${}^5\Sigma$ state observed in experiment is ${}^5\Sigma^+$. We also note that at the CASSCF level, the ${}^5\Pi - {}^5\Sigma^+$ transition moment is significantly larger than the ${}^5\Pi - {}^5\Sigma^-$ transition moment. The ${}^5\Delta$ T_e value is in reasonable agreement with experiment, but the computed ω_e value is significantly larger than the experimental value, which was described³ as “less certain”.

In the lower part of Table I we compare our computed results with the experimental results from the photodetachment spectra². For CrO⁻, our ${}^6\Sigma^+ - {}^4\Pi$ separation of 0.12 eV is in excellent agreement with experiment (0.096 ± 0.006 eV), but the assignment of the states is reversed. Our computed ω_e values of 764 cm⁻¹ for the ${}^6\Sigma^+$ state and 871 cm⁻¹ for the ${}^4\Pi$ state are consistent with experiment, where the lower of the two observed states has a frequency of 885 ± 80 cm⁻¹ and the upper state has a

frequency of $780 \pm 80 \text{ cm}^{-1}$, and therefore the ω_e values support our assignment. We should note that at the CASSCF level the ${}^4\Phi$ state is much higher in energy than the ${}^6\Sigma^+$ state and we do not consider it as a candidate for the low-lying excited state of CrO^- .

We summarize the orbital occupations in Table II. We also show which neutral states will arise from one electron detachment processes from the two anion states. The assignment of the ${}^5\Pi$ state as arising from the 1.22 eV detachment transition from the ${}^4\Pi$ state and 1.12 eV detachment from the ${}^6\Sigma^+$ state seem well established, and therefore we shift our computed detachment energies to agree with these experimental values. After this shift, it is clear that the 1.82 eV detachment energy, must correspond to the ${}^4\Pi \rightarrow {}^3\Sigma^-$ process: our shifted energy and computed vibrational frequencies agree well with experiment. Thus we agree with Wang and co-workers that the lowest excited state is ${}^3\Sigma^-$ (n.b. this state was mislabeled ${}^3\Sigma^+$ in Reference 2). While this detachment is a one-electron process, it is surprisingly weak.

The experimental transition at 2.13 eV is assigned as ${}^6\Sigma^+ \rightarrow {}^5\Sigma^+$. The shifted energy, especially if corrected using the experimental ${}^5\Sigma^+ - {}^5\Pi$ excitation energy, agrees very well with experiment. The assignment of Wang and co-workers to the ${}^5\Delta$ state is inconsistent with the location of the ${}^5\Delta$ state obtained from our calculations or the optical experiments. The experimental vibrational frequency is much smaller than our computed value or that from the optical experiments. We suspect the experimental ω_e value is in error since there do not appear to be any states with a frequency that low in this energy region.

The transition at 2.26 eV is assigned as ${}^4\Pi \rightarrow {}^3\Pi$ as done by Lineberger and co-workers, and not as assigned by Wang and co-workers. The ${}^4\Pi \rightarrow {}^3\Pi$ is a one-electron process and is therefore expected to be strong. The computed vibrational frequency supports this assignment. The 2.64 eV transition is assigned as ${}^6\Sigma^+ \rightarrow {}^5\Delta$. While the ${}^6\Sigma^+ \rightarrow {}^3\Delta$, ${}^4\Pi \rightarrow {}^3\Delta$, and ${}^4\Pi \rightarrow {}^5\Delta$ transitions have similar energies, only

the ${}^6\Sigma^+ \rightarrow {}^5\Delta$, is a one-electron process. While our assignment is not definitive, we feel that we can rule out the ${}^3\Pi$ state suggested by Wang and co-workers since our calculations show that the ${}^3\Pi$ state is much lower in energy.

The 3.03 eV transition is assigned as ${}^4\Pi \rightarrow {}^3\Phi$, as was done by Wang and co-workers. Our computed vibrational frequency is in reasonable with experiment and this transition corresponds to a one-electron process. The error (0.14 eV) in the computed detachment energy is of the same size as observed for the ${}^5\Sigma^+$ state. Thus the assignment of this transition is tentative like that for the 2.64 eV transition. Supporting our current assignment is the fact that all 7 of the observed transitions are assigned as arising from one-electron detachment processes.

IV. CONCLUSIONS

We assign the ground state of CrO^- as ${}^4\Pi$; this is consistent with that of Lineberger and co-workers, but disagrees with the assignment of Wang and co-workers. We assign the low-lying excited state as ${}^6\Sigma^+$. Thus, like Wang and co-workers, we find the two lowest states to be ${}^4\Pi$ and ${}^6\Sigma^+$, but we find the opposite ordering. The agreement between the computed and experimental vibrational frequencies supports our assignment. The seven observed transitions in the photodetachment spectra are assigned to one-electron detachment process from the two anion states. Our assignment for the neutral states differs from that of Wang and-coworkers.

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REFERENCES

- ¹ P. G. Wenthd, R. F. Gunion, and W. C. Lineberger, *Chem. Phys. Lett.* **258**, 101 (1996).
- ² G. L. Gutsev, P. Jena, H.-J. Zhai, and L.-S. Wang, *J. Chem. Phys.* **115**, 7935 (2001).
- ³ T. C. Devore and J. L. Gole, *Chem. Phys.* **133**, 95 (1989).
- ⁴ A. S-C. Cheung, W. Zyrnicki, and A. J. Merer, *J. Mol. Spectrosc.* **104**, 315 (1984).
- ⁵ H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988).
- ⁶ P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988.)
- ⁷ C. W. Bauschlicher, *Theor. Chim. Acta*, **92**, 183 (1995).
- ⁸ T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ⁹ R. A. Kendall, T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ¹⁰ MOLPRO is a package of *ab initio* programs written by H.-J. Werner, and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Llyod, W. Meyer, A. Nicklass, K Peterson, R., Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schütz, H Stoll, and T. Thorseinsson.

TABLES

TABLE I. Summary of computed results for CrO and CrO⁻.

State	IC-MRCI+Q			Experiment ^a		
	$r_e(\text{\AA})$	$\omega_e(\text{cm}^{-1})$	$T_e(\text{cm}^{-1})$	$r_0(\text{\AA})$	$\Delta G_{1/2}(\text{cm}^{-1})$	$T_0(\text{cm}^{-1})$
³ Φ	1.600	975	15789			
⁵ Δ	1.653	892	12492		820 ³	$\approx 11800^3$
³ Δ	1.562	1020	11795			
³ Π	1.620	917	7998			
⁵ Σ^-	1.680	811	7482			
⁵ Σ^+	1.671	894	6967	1.662	868	8191
³ Σ^-	1.618	889	5378			
⁵ Π	1.629	879	0	1.621	885	0
⁶ Σ^+	1.704	764				
⁴ Π	1.647	871				

State	⁴ Π detachment (eV)		$\omega_e(\text{cm}^{-1})$		⁶ Σ^+ detachment (eV)	
	IC-MRCI+Q ^b	Expt ²	Expt ²	Expt ¹	IC-MRCI+Q ^c	Expt ²
³ Φ	3.17	3.03	920 \pm 80	920 \pm 80	3.07	
⁵ Δ	2.77				2.67	2.64
³ Δ	2.68				2.58	
³ Π	2.21	2.26	950 \pm 80	960 \pm 40	2.11	
⁵ Σ^-	2.14				2.04	
⁵ Σ^+	2.08			715 \pm 60	1.98 ^d	2.13
³ Σ^-	1.88	1.82	940 \pm 60	945 \pm 40	1.78	
⁵ Π	1.22	1.22	920 \pm 80	885 \pm 20	1.12	1.12
⁶ Σ^+	0.12	0.096 \pm 0.050	780 \pm 80			
⁴ Π	0.00	0.00		885 \pm 80		

^a Reference 4 unless otherwise noted.

^b Shifted by 0.43 eV.

^c Shifted by 0.45 eV.

^d Using the experimental ⁵ Σ^+ - ⁵ Π separation yields 2.13 eV.