

Ultraviolet negative-ion photoelectron spectroscopy of the chromium oxide negative ion

Paul G. Wenthold, Robert F. Gunion, W.C. Lineberger

JILA, National Institute of Standards and Technology, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440, USA

Received 7 May 1996; in final form 8 May 1996

Abstract

The photoelectron spectrum of CrO^- is reported, with four electron states of CrO detected. The $^5\Pi$ ground state of CrO has an electron affinity of 1.221 ± 0.006 eV. An excited $^3\Pi$ state is also observed, which lies 8600 ± 40 cm^{-1} above the ground state. Two additional states of CrO , believed to be triplets, are observed at energies of 4835 ± 80 and 7365 ± 40 cm^{-1} , respectively.

1. Introduction

Experimental and theoretical studies of metal oxides such as CrO are often challenging because the d orbitals give rise to many low-lying electronic states with different possible spin states, many of which are invisible to standard optical spectroscopy. The physical characteristics of chromium oxide have especially been of considerable interest. The ground state of CrO has been assigned to be $^5\Pi$ on the basis of the work by Hocking et al. [1] and ab initio calculations by Bauschlicher et al. [2]. Large-scale multireference configuration interaction calculations have been carried out by Bauschlicher et al. [2] and Jasien and Stevens [3] on the ground state. From their calculations, they predict a bond length in the range of 1.65–1.66 Å and $\omega_e = 820$ – 850 cm^{-1} , in reasonable agreement with the experimental values of $R_e = 1.618$ and $\omega_e = 898.5$ cm^{-1} , determined using rotationally resolved laser-induced fluorescence [1]. The vibrational frequency for $X^5\Pi$ CrO has been measured to be 885 cm^{-1} [1,4]. Using intermodu-

lated fluorescence spectroscopy, Steimle et al. [5] have measured the dipole moment of CrO to be 3.88 ± 0.13 D, while the dissociation energy has been estimated to be 104.3 ± 2.1 kcal/mol from the enthalpy of oxygen atom exchange reactions between Cr and WO_3 and EuO [6]. The ionization potential of CrO has been found to be 7.85 ± 0.02 eV using photoelectron spectroscopy [7].

Excited electronic states of CrO have been observed at energies of 8191.23 [4], 11800 [8], and 16502.4 cm^{-1} [1] above the ground state. These have been assigned to the $^5\Sigma^+$, $^5\Delta$, and $^5\Pi$ states, respectively. A second excited $^5\Pi$ state has also been found at 22163 cm^{-1} . However, although these states have been reasonably well characterized, little is known experimentally about the other spin states of CrO , such as the triplet or septet states.

Additional information about the excited states of the CrO molecule has come from theoretical calculations. Bauschlicher et al. [2] have calculated energies and vibrational frequencies for the $^5\Sigma^+$, $^7\Pi$, and $^7\Sigma$ of CrO in addition to the $X^5\Pi$ state. At the CASSCF

Two intense features are observed in the spectra for these ions, corresponding to electron detachment from the doubly occupied $4s$ and $5s\sigma$ orbitals, respectively. For CrO^- , detachment from the $4s\sigma^2$ orbital should be the predominant process, leading to formation of the $X^5\Pi$ and $^3\Pi$ states of CrO . Detachment to form other triplet or quintet states of CrO is possible but expected to be weaker.

The 351 nm photoelectron spectrum of CrO^- is shown in the bottom half of Fig. 2. For comparison, the photoelectron spectrum of Cr^- , similar to that described previously [11], is also shown. The two expected strong features are immediately apparent, but three weaker electronic transitions are also observed in the CrO^- spectrum. The origins of the bands are marked as A, B, C, D, and E in Fig. 2, and the positions of the origin peaks are listed in Table 1, along with the vibrational splittings for each state.

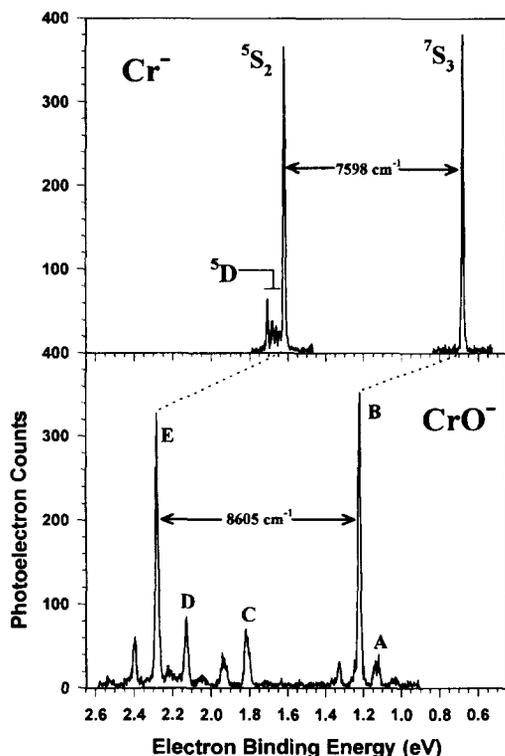


Fig. 2. 351 nm photoelectron spectra of Cr^- (top) and CrO^- (bottom). The energy splittings between the 7S and 5S states of Cr and the $^5\Pi$ and $^3\Pi$ states of CrO are indicated to emphasize the comparison.

Table 1

Relative energies and vibrational frequencies for electronic states of CrO^- and CrO ^a

Band ^b	State	Relative energy ^c	Vibrational frequency
CrO^-			
A	$X^4\Pi$	0	885 ± 80 ^d
	$A^4\Phi$	750 ± 80	–
CrO			
B	$X^5\Pi$	0	885 ± 20
C		4835 ± 80	945 ± 40
D		7365 ± 40	715 ± 60 ^e
E	$^3\Pi$	8600 ± 40	960 ± 40

^a Energies in cm^{-1} , unless otherwise marked.

^b Photoelectron band as labeled in Fig. 2.

^c Energy of the origin relative to the ground state of CrO^- or CrO .

^d Obtained from vibrational hot band for band C.

^e This peak may also correspond to a two-electron transition from CrO^- to the $^5\Sigma$ state of CrO .

The features labeled B and E dominate the spectrum, and correspond to formation of the $X^5\Pi$ and $^3\Pi$ states of CrO , respectively. Band A is most likely due to transitions from a long-lived electronically excited state of the ion, while the features labeled C and D are most likely due to formation of low-lying triplet states of CrO .

3.1. $^5\Pi$ and $^3\Pi$ states

The two largest peaks in the spectrum of CrO^- correspond to formation of the $^5\Pi$ and $^3\Pi$ states of CrO . This assignment is based in part on a comparison with the spectrum of Cr^- , shown in the top half of Fig. 2. The two largest peaks in the Cr^- spectrum correspond to formation of the 7S and 5S states of Cr , resulting from detachment from the doubly occupied $4s$ orbital [11]. The $^5\Pi$ and $^3\Pi$ states of CrO are formed in a similar fashion by detachment from the doubly occupied $4s\sigma$ orbital of CrO^- . This assignment is supported by angular distribution studies, which indicate that the features are due to detachment from an s-like (σ) orbital (vide infra). The energy splitting between the $^5\Pi$ and $^3\Pi$ states is 8600 cm^{-1} , only 1000 cm^{-1} higher than the 7S – 5S splitting in Cr [12]. This indicates that the presence of the oxygen atom does not have a large impact on

the energies of the 4s orbitals in Cr, consistent with the MO diagram shown in Fig. 2.

Vibrational frequencies for both the $^5\Pi$ and $^3\Pi$ states can be obtained from the spectrum shown in Fig. 2. For the $^5\Pi$ state, we find a vibrational frequency of 885 cm^{-1} , which agrees perfectly with previously reported values [1,4]. A vibrational frequency of 960 cm^{-1} is found for the $^3\Pi$ state of CrO. No other experimental or theoretical information is available for this state.

There are additional transitions observed in the vicinity of the $^5\Pi$ state, marked as A in Fig. 2. These appear to be hot bands, but are too intense to be vibrational hot bands. More likely, band A is due to transitions from a long-lived electronically excited state of CrO^- to the ground state of CrO. This ion is possibly the $^4\Phi$ state, with a $4s\sigma^1 3d\delta^3 3d\pi^1$ configuration (Fig. 1). From the splitting between peaks A and B, this state lies $\approx 750\text{ cm}^{-1}$ higher in energy than the $^4\Pi$ state. From the hot band for feature A, we obtain a vibrational frequency of 750 cm^{-1} for the $^4\Phi$ state of the ion. The transitions from the excited state of the CrO^- ion to the $^5\Pi$ state of CrO are significantly broader than those from the ground state. This is most likely due to spin-orbit coupling in the $^4\Phi$ state, which is too small to be completely resolved. For this reason, the uncertainties for the quantities listed above are slightly larger ($\pm 80\text{ cm}^{-1}$). Transitions from the $^4\Phi$ state of CrO^- to the $^3\Pi$ state of CrO would be two-electron transitions, and are too weak to be observed.

3.2. Other electronic states

In addition to the intense peaks corresponding to formation of the $^5\Pi$ and $^3\Pi$ states, weaker transitions to two other states of CrO are also observed. The origins of these states are marked as C and D, and they lie 4835 ± 80 and $7365 \pm 40\text{ cm}^{-1}$ above the ground state, respectively. These do not correspond to previously known states of CrO and are most likely due to formation of triplet states which would be inaccessible using optical spectroscopy of CrO. The intensities of bands C and D indicate that they likely arise from one-electron transitions from CrO^- , i.e. they result from simple photodetachment. Possible triplet states that can be formed by direct detachment from CrO include a $^3\Sigma$ state ($3d\delta^2 4s\sigma^2$) from

detachment of a π electron, and a $^3\Phi$ state ($3d\delta^1 3d\pi^1 4s\sigma^2$) formed by detachment of a δ electron. Neither of these states could be accessed by direct detachment from the $^4\Phi$ state of CrO^- .

Vibrational structure is apparent for bands C and D. Band C consists of an extended vibrational progression with an average spacing of 940 cm^{-1} between the peaks. As was found with band A, the peaks of band C are broadened due to unresolved split-orbit coupling. A vibrational hot band is observed for band C at an energy that is 885 cm^{-1} from the origin. This is the vibrational frequency for the $^4\Pi$ state of CrO^- .

The feature labeled D consists of a sharp peak with what appears to be a weak vibration at 715 cm^{-1} . However, the vibrational level is about 8100 cm^{-1} higher in energy than the origin of the $^5\Pi$ state, in approximately the region where the $^5\Sigma$ state ($3d\delta^2 3d\pi^2$) would be expected to be observed [4]. Moreover, the intensity of this peak is very weak, consistent with what is expected for the two electron transition required to form the $^5\Sigma$ state. Therefore, it is possible that this small peak is either a vibrational peak for band D, a weak two-electron transition to the $^5\Sigma$ state, or a combination of both.

Unfortunately, there are no previous experimental or theoretical studies of the triplet states of CrO, as the only information available for the non-quintet states of CrO comes from the theoretical calculations by Baushlicher et al. [2] on the septet states. The results obtained in the present study indicate that the triplet states of CrO are sufficiently low in energy to warrant further investigation.

3.3. Angular distribution measurements

The intensity of photodetachment of electrons is dependent upon the polarization of the laser and, therefore, angular distributions can provide additional information about the CrO^- molecule. The angular distribution of photoelectron detachment is measured by varying the angle of the electric field vector of the laser with respect to the direction of the electron detector. The intensity of the photoelectron detachment for atoms is described by Eq. (1) [13,14],

$$I_{\theta} = 1 + \beta P_2(\cos \theta), \quad (1)$$

where $P_2(\cos \theta)$ is the second associated Legendre polynomial and β is an anisotropy parameter which can range over $-1 \leq \beta \leq 2$. The parameter β provides information regarding the orbital from which the electron is detached. Electrons detached from atomic s orbitals will have p-wave character, resulting in $\beta = +2$. Similarly, detachment from p orbitals results in a combination of s-wave and d-wave detachment. Near threshold, s-wave detachment dominates giving $\beta = 0$, but at higher energies, d-wave detachment becomes more predominant and β approaches -1 . For d electrons, p- and f-wave detachment occurs, with p-wave dominant near threshold, giving β near $+2$. For molecular systems, interpretation of the anisotropy parameter is more complicated. However, it has been observed that electrons originating in diffuse σ orbitals give $\beta = 1.5$ – 2.0 , while detachment from π (p-like) orbitals leads to $\beta < 0$. Detachment from δ orbitals will tend to result in $\beta > 0$.

The spectra in Fig. 2 were measured at the ‘magic angle’ (54.7°) for which $P_2(\cos \theta) = 0$ so that the relative intensities of detachment were equal for all electrons. Spectra of Cr^- and CrO^- were also taken at parallel (I_0) and perpendicular (I_{90}) polarizations and the anisotropy parameters for each peak was determined using the relationship $\beta = (I_0 - I_{90}) / (0.5I_0 + I_{90})$. For Cr^- $\beta = 2$ for the 5S_2 and 7S_3 peaks indicating that they were detached from an s orbital. For the CrO^- molecule $\beta = 1.4 \pm 0.2$ for detachment to give the $^3\Pi$ state and $\beta = 1.7 \pm 0.2$ for detachment to the $^5\Pi$ state, indicating that both of these electrons were detached from an almost spherical σ orbital. The intensities of the remaining peaks in the CrO^- spectra are much lower than the $^3\Pi$ and $^5\Pi$ origins and therefore the anisotropy parameters cannot be determined with the same degree of certainty. Approximate values of 0.6, -0.2 , and 1.4 are found for the origin peaks of A, C, and D, respectively.

3.4. Thermochemistry

Not only can the photoelectron spectrum of CrO^- be used to determine the electron affinity (EA) of the species, but information from it can be used to infer more about the character of the Cr–O bond. The electron affinity measured for CrO can be used to

derive evidence for the non-bonding character of the σ orbital which the extra electron in CrO^- occupies. The electron affinity of CrO, 1.221 ± 0.006 eV, is much closer to that of oxygen (EA = 1.4611 eV) than it is to Cr (EA = 0.678 ± 0.004 eV, Fig. 2) [11]. The Cr–O $^-$ bond energy, $D_0(\text{Cr–O}^-)$ can be calculated from the bond energy in CrO and the electron affinities of CrO and oxygen according to

$$D_0(\text{Cr–O}^-) = D_0(\text{Cr–O}) + \text{EA}(\text{CrO}) - \text{EA}(\text{O}). \quad (2)$$

The Cr–O $^-$ bond energy calculated using Eq. (2) is 98.8 ± 2.1 kcal/mol, 5 kcal/mol lower than the bond in neutral CrO [6]. This indicates that the extra electron in CrO resides in a largely non-bonding orbital.

Acknowledgements

This project was carried out as part of a special project involving undergraduate students in the Physical Chemistry Laboratory class at the University of Colorado. The members of the class who participated in this project and carried out the work are Sean Feree, Hyun Lee, Scott McEntyre, Blue Parish, Meghan Peckis, Jennifer Shull, Carrie Swartz, Michael Turpin, and Michael Zinkovitch. Funding for this project was provided by the National Science Foundation (PHY-9512150, CHE-9318639).

References

- [1] W.H. Hocking, A.J. Merer, D.J. Milton, W.E. Jones and G. Krishnamurty, *Can. J. Phys.* 58 (1980) 516.
- [2] C.W. Bauschlicher, C.J. Nelin and P.S. Bagus, *J. Chem. Phys.* 82 (1985) 3265.
- [3] P.G. Jasien and W.J. Stevens, *Chem. Phys. Lett.* 147 (1988) 72.
- [4] A.S.C. Cheung, W. Zyrnicki and A.J. Merer, *J. Mol. Spectrosc.* 104 (1984) 315.
- [5] T.C. Steimle, D.F. Nachman, J.E. Shirley, J.C.W. Bauschlicher and S.R. Langhoff, *J. Chem. Phys.* 91 (1989) 2049.
- [6] G. Balducci, G. Gigli and M. Guido, *J. Chem. Soc. Faraday Trans.* 2 77 (1981) 1107.
- [7] J.M. Dyke, B.W.J. Gravenor, R.A. Lewis and A. Morris, *J. Chem. Soc. Faraday Trans.* 2 (1983) 1083.
- [8] T.C. Devore and J.L. Gole, *Chem. Phys.* 133 (1989) 95.

- [9] R.F. Gunion, S.J. Dixon-Warren, W.C. Lineberger and M.D. Morse, *J. Chem. Phys.* (1996) in press.
- [10] K.M. Ervin and W.C. Lineberger, in: *Photoelectron spectroscopy of negative ions*, eds. N.G. Adams and L.M. Babcock (JAI Press, Greenwich, CT, 1992).
- [11] A.A. Bengali, S.M. Casey, C. Chun-Lin, J.P. Dick, P.T. Fenn, P.W. Villalta and D.G. Leopold, *J. Am. Chem. Soc.* 114 (1992) 5257.
- [12] C.E. Moore, *Atomic energy levels* (US GPO Circular No. 467, Washington, DC, 1952).
- [13] J. Cooper and R.N. Zare, *J. Chem. Phys.* 48 (1968) 942.
- [14] J. Cooper and R.N. Zare, *J. Chem. Phys.* 49 (1968) 4252.