

The electronic structure of MoC and WC by anion photoelectron spectroscopy

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Photoelectron spectra of MoC⁻ and WC⁻ are reported at two detachment energies, 532 and 355 nm. The electron affinities of MoC and WC were measured to be 1.358 (0.010) and 1.022 (0.010) eV, respectively. Seven low-lying electronic states were observed for MoC within 2 eV above its ground state whereas six were observed for WC within 2.4 eV above its ground state. The bonding and spectroscopy of MoC and WC were found to be different and were attributed to their different atomic configurations due to the strong relativistic effects in W. The current study reports the first spectroscopic information on WC. © 1999 American Institute of Physics.

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I. INTRODUCTION

The chemical bonding between transition metals and carbon is important in several areas of chemistry, such as organometallic chemistry, surface chemistry, catalysis, and astrochemistry. Diatomic metal carbides are the simplest systems to understand the metal-carbon chemical bonding. Indeed, increasing theoretical and experimental efforts have recently been focused on these systems.¹ However, very few carbide diatomics involving the 5*d* transition metals have been studied. There have been experimental studies for only two 5*d* carbides, PtC and IrC,²⁻⁴ and theoretical studies for only TaC and IrC.^{5,6} Most of the experimental investigations on diatomic carbide species have involved optical techniques,¹⁻⁴ which are powerful to yield detailed spectroscopic information about electronic states allowed in optical transitions. However, a high density of low-lying electronic states are expected for the transition metal species and many of these states are not accessible to optical experiments, either their excitation energies are too low or they are not allowed optical transitions. We have shown that photoelectron spectroscopy (PES) of anion species is an ideal experimental technique to map out the low-lying states of these complicated electronic systems.⁷⁻⁹ In this article, we report our PES investigation on MoC and WC.

There has been no experimental or theoretical study available for WC. The first spectroscopic investigation of MoC has been just reported by Morse and co-workers,¹⁰ who also provided an excellent discussion of the chemical bonding between the 4*d* transition metals and C and its trend across the periodic table. Due to the strong relativistic effects, the 5*d* transition metals are expected to show different behaviors in their bonding to C. We obtained vibrationally resolved PES spectra of MoC⁻ and WC⁻ at two photon energies, 532 (2.331 eV) and 355 nm (3.496 eV). The electron affinities (EAs) of MoC and WC were determined to be

1.358 (0.010) and 1.022 (0.010) eV, respectively. Seven low-lying electronic states for MoC and six for WC were observed and tentatively assigned. The chemical bonding in the two diatomics is discussed and compared.

II. EXPERIMENT

All experiments were performed with a magnetic-bottle time-of-flight (TOF) PES apparatus and a laser vaporization supersonic cluster source, which had been published in detail previously.^{7,11} Only a brief description is given here. The MoC⁻ anion was produced from plasma reactions between laser ablated molybdenum atoms and CH₄ seeded in a He carrier gas containing 5% CH₄ while the WC⁻ anion was produced by direct laser ablation of a tungsten carbide (WC) target with a pure He carrier gas. Besides the desired MoC⁻ and WC⁻ diatomic species, other larger clusters were also formed with their relative abundance depending on the source conditions. The clusters formed in the source were expanded to form a supersonic cluster beam which was collimated by a 6 mm diameter skimmer. Anionic species were extracted perpendicularly from the beam by a high voltage pulse, and were analyzed by a TOF mass spectrometer. The resolution of the mass spectrometer was sufficient to resolve the different isotopes of Mo and W in MoC⁻ and WC⁻. After being mass selected and decelerated, the desired anions were crossed with a detachment laser beam in the detachment zone of the magnetic-bottle electron analyzer. The third or second harmonic of a Nd:YAG laser (355 and 532 nm) were used for photodetachment in the current investigation. Photoelectrons were collected by the magnetic bottle at nearly 100% efficiency and analyzed by a 3.5 m long TOF flight tube. The absolute electron kinetic energies were calibrated and converted from the measured TOF spectra using the known spectra of Rh⁻.¹² The electron kinetic energy resolution in the present study was better than 30 meV (FWHM) for 1 eV electrons.

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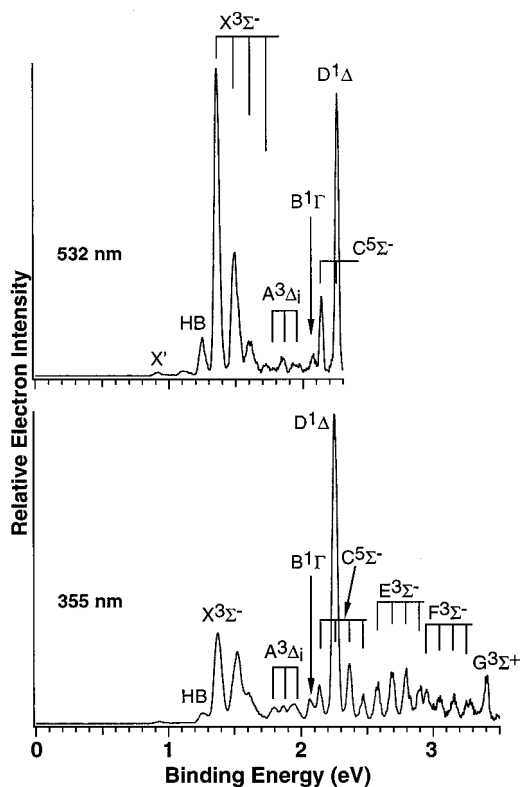


FIG. 1. Photoelectron spectra of MoC⁻ at 532 (2.331 eV) and 355 nm (3.496 eV) and their assignments. HB represents hot band transitions.

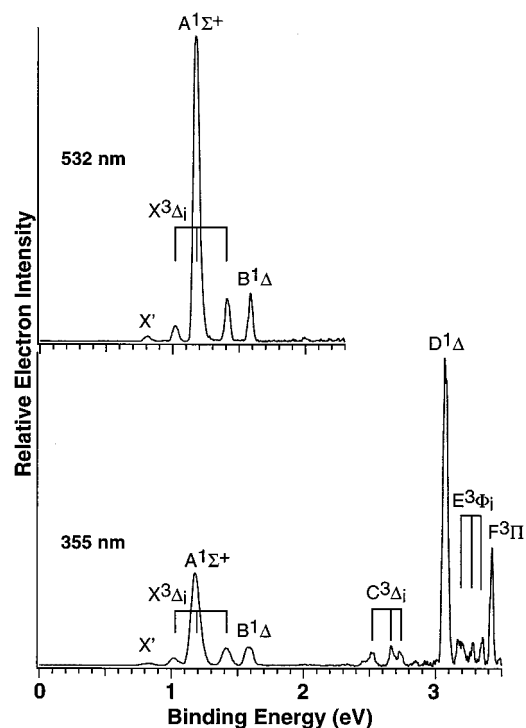


FIG. 2. Photoelectron spectra of WC⁻ at 532 (2.331 eV) and 355 nm (3.496 eV) and their assignments.

III. RESULTS AND DISCUSSION

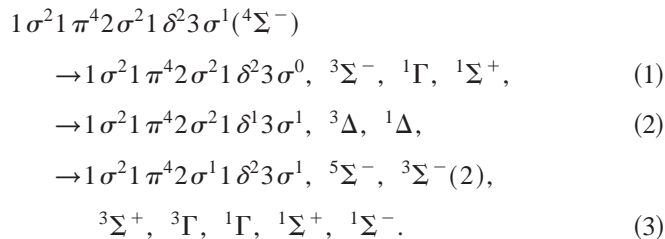
The PES spectra of MoC⁻ and WC⁻ at 532 and 355 nm are shown in Figs. 1 and 2, respectively. Well-resolved spectra were obtained for both species. The spectral features of MoC⁻ appeared much more complicated than that of WC⁻. The PES spectra represent transitions from the ground states of the anions to the ground and low-lying excited states of the neutral molecules. Excitation energies of the low-lying excited states can be obtained straightforwardly from the binding energy differences between that of the excited states and that of the ground state. The identified electronic states and their assignments are labeled in the figures and the binding energies of each feature and the derived spectroscopic constants are given in Tables I and II for MoC and WC, respectively. As will be subsequently discussed, some of the assignments are rather tentative, in particular, for those of WC, for which no prior experimental or theoretical work exists.

A. MoC

MoC has been studied both experimentally^{10,13} and theoretically.¹⁴ Its ground electronic state is known to be $^3\Sigma^-$ with a vibrational frequency calculated to be 997 cm^{-1} . The ground state properties of MoC have been well discussed by Morse *et al.* in their recent spectroscopic investigation.¹⁰ Figure 3 shows schematically the valence molecular orbitals (MOs) of MoC and the ground state configuration, $1\sigma^2 1\pi^4 2\sigma^2 1\delta^2$, where $1\sigma^2$ is mainly the C $2s$,

1π and 2σ are bonding MOs between C $2p$ and Mo $5d$, 1δ and 3σ are nonbonding MOs from Mo $4d$ and $5s$, respectively.

In the MoC⁻ anion, the extra electron can either enter the 1δ MO to give a $1\delta^3$ configuration or the 3σ MO to give a $1\delta^2 3\sigma^1$ configuration, depending on the separation between the 1δ and 3σ MOs. If that separation is larger than the electron–electron repulsion introduced by adding an electron into the 1δ MO, the $1\delta^3$ configuration would be favored. If the separation between the 1δ and 3σ MOs is not too large, the $1\delta^2 3\sigma^1$ configuration would be favored. For the latter configuration, the electron–electron repulsion is reduced as compared to the $1\delta^3$ configuration, and additional stabilization is expected in the $^4\Sigma^-$ state due to favorable exchange interaction. Given these considerations, we assume that the MoC⁻ anion has the $1\delta^2 3\sigma^1$ configuration with a $^4\Sigma^-$ electronic state. From this anion configuration, the following detachment channels are expected:



Depending on the photon energies, other detachment channels with high binding energies can also occur. We expect that the removal of a 2σ bonding electron would weaken the MoC bonding and give rise to broad vibrational progressions for the electronic states with this configuration whereas the

TABLE I. Observed binding energies (BE) and spectroscopic constants of MoC from photoelectron spectra of MoC⁻.

	BE (eV)	Term value (eV)	Vib. freq. (cm ⁻¹)
$X^3\Sigma^- (1\sigma^2 1\pi^4 2\sigma^2 1\delta^2 3\sigma^0)$	1.358 (0.010)	0	1000 (100)
$A^3\Delta_1 (1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^1)$	1.798 (0.020)	0.440 (0.020)	
$^3\Delta_2$	1.864 (0.020)		
$^3\Delta_3$	1.948 (0.030)		
$B^1\Gamma (1\sigma^2 1\pi^4 2\sigma^2 1\delta^2 3\sigma^0)$	2.070 (0.020)	0.712 (0.020)	
$C^5\Sigma^- (1\sigma^2 1\pi^4 2\sigma^1 1\delta^2 3\sigma^1)$	2.138 (0.010)	0.780 (0.10)	
$D^1\Delta (1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^1)$	2.256 (0.010)	0.898 (0.010)	890 (60)
$E^3\Sigma^- (1\sigma^2 1\pi^4 2\sigma^1 1\delta^2 3\sigma_1)$	2.584 (0.010)	1.226 (0.010)	(890)
$F^3\Sigma^- (1\sigma^2 1\pi^4 2\sigma^1 1\delta^2 3\sigma^1)$	2.950 (0.010)	1.592 (0.010)	870 (60)
$G^3\Sigma^+ (1\sigma^2 1\pi^4 2\sigma^1 1\delta^2 3\sigma^1)$	3.400 (0.020)	2.042 (0.020)	850 (60)

removal of a 1δ electron should lead to sharp features with little vibrational excitation due to its nonbonding nature.

The 532 nm spectrum of MoC⁻ displayed a strong peak at 1.358 eV with a well resolved vibrational progression which has a spacing of about 1000 cm⁻¹. This progression is assigned to be the ground state of MoC ($^3\Sigma^-$) resulting from removing the 3σ electron (1). The observed vibrational spacing is consistent with the vibrational frequency calculated for the ground state of MoC.¹⁴ The adiabatic EA of MoC is defined by the 1.358 eV peak, which is the 0–0 transition. The two weak features immediately to the left of the 0–0 transition should be due to vibrational hot bands of the anion, yielding a vibrational frequency of 870 (80) cm⁻¹ for MoC⁻. The very weak feature at about 0.92 eV (X' , Fig. 1) was likely due to an electronically excited state of MoC⁻. Both the observations of a smaller vibrational frequency for MoC⁻ and the ground state vibrational progression suggest that the 3σ orbital is slightly antibonding.

At 355 nm, we observed that the intensity of the ground state features were significantly reduced. Furthermore, the vibrational progression of the ground state appeared to be quite different: the intensity of the 0→1 peak was enhanced relative to the 0–0 peak and the spacing between the two peaks was increased. There are two possibilities for this observation: (1) there was another electronic state that overlapped with the 0→1 peak and its intensity was enhanced at 355 nm; (2) there was an autodetachment state for MoC⁻ at 355 nm that could result in unusual Franck–Condon factors.

TABLE II. Observed binding energies (BE) and spectroscopic constants of WC and from photoelectron spectra of WC⁻.

	BE (eV)	Term value (eV)
$X^3\Delta_1 (1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^1)$	1.022 (0.010)	0
$^3\Delta_2$	1.174 (0.010)	
$^3\Delta_3$	1.410 (0.010)	
$A^1\Sigma^+ (1\sigma^2 1\pi^4 2\sigma^2 3\sigma^2)$	1.174 (0.010)	0.152 (0.010)
$B^1\Delta (1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^1)$	1.585 (0.010)	0.563 (0.010)
$C^3\Delta_1 (1\sigma^2 1\pi^4 2\sigma^1 1\delta^1 3\sigma^2)$	2.522 (0.020)	1.500 (0.020)
$^3\Delta_2$	2.666 (0.015)	
$^3\Delta_3$	2.724 (0.015)	
$D^1\Delta (1\sigma^2 1\pi^4 2\sigma^1 1\delta^1 3\sigma^2)$	3.071 (0.010)	2.049 (0.020)
$E^3\Phi_2 (1\sigma^2 1\pi^3 2\sigma^2 1\delta^1 3\sigma^2)$	3.196 (0.010)	2.174 (0.020)
$^3\Phi_3$	3.276 (0.010)	
$^3\Phi_4$	3.354 (0.010)	
$F^3\Pi (1\sigma^2 1\pi^3 2\sigma^2 1\delta^1 3\sigma^2)$	3.426 (0.010)	2.404 (0.020)

The latter might be the case since there is no known excited state for MoC with such a low excitation energy. The lowest excited state calculated by Shim and Gingerich is at 4500 cm⁻¹.¹⁴

The 532 nm spectrum shows several weak features [(A) and (B)] beyond the ground state vibrational progression and two strong peaks at 2.138 (C) and 2.256 eV (D). The intensity of the 2.256 eV feature was significantly enhanced at 355 nm; the intensities of the weak features [(A) and (B)] observed at 532 nm were also slightly enhanced at 355 nm. The intensity of the 2.138 eV feature relative to the ground state 0–0 feature was unchanged at 355 nm. The three weak features (A) between 1.8 and 2 eV appeared to be due to spin-orbit splittings and were assigned to the $^3\Delta$ state due to removal of a 1δ electron (2). The separations among the three components were comparable to the spin-orbit splitting in atomic Mo.¹⁵ Since the 1δ MO is nonbonding, no vibrational structure was expected, consistent with the observation of only the three spin-orbit features. However, the very weak intensity of this transition is puzzling. As shown in Eq. (2), a $^1\Delta$ state was also expected from the removal of a 1δ electron. The very strong peak at 2.256 eV was assigned to this state. The features around this strong peak were assigned to the $^5\Sigma^-$ state and will be discussed below. The enhancement of the intensities of the $^3\Delta$ and $^1\Delta$ features at 355 nm was expected. However, their considerable intensity disparity

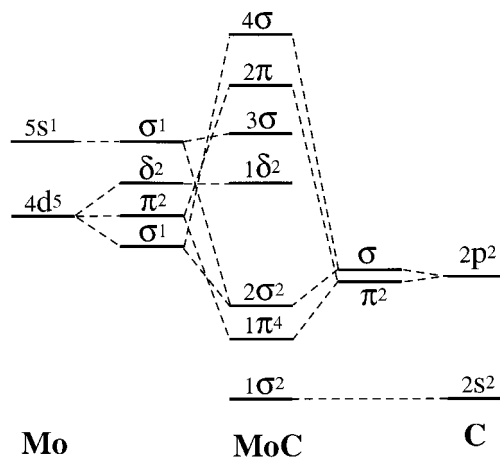


FIG. 3. A schematic valence molecular orbital diagram for MoC.

was not understood. We expected that the triplet features should have a slightly higher intensity than the singlet. As will be seen below, the $^1\Delta$ feature was overlapped with the $\nu=1$ feature of the $^5\Sigma^-$ state but that was not sufficient to account for its apparently anomalous intensity.

The peak at 2.07 eV (B) is a lone feature: its separation from the 2.138 eV peak is too small to be accounted as a component of a vibrational progression. We tentatively assigned this feature to be the $^1\Gamma$ state, derived from the same configuration as the ground state Eq. (1). The weak intensity was expected because this state was not allowed in the single particle approximation. It had to be derived from the removal of the 3σ electron accompanied by the change of a quantum number of a 1δ electron, i.e., it should be considered as a ‘‘shakeup’’ feature.¹⁶ Its presence in the PES spectra indicates strong electron correlation effects in the ground state of the anions.

At first glance the 2.138 eV peak (C) might be considered to be part of a vibrational progression including the strong peak at 2.256 eV. However, the intensity of the 2.138 eV peak at 355 nm was not correlated with the 2.256 eV peak, suggesting that the 2.138 and 2.256 eV peaks represent two different electronic states. The 355 nm spectrum revealed many more well resolved features beyond the 532 nm spectrum. In particular, two peaks at 2.364 and 2.468 eV were observed which might be considered as part of a vibrational progression with the strong peak at 2.256 eV as the 0–0 transition. The 2.138 eV peak could then be viewed as a hot band for this progression. However, as we discussed above, the 2.138 eV peak was independent of the 2.256 eV peak. We noticed that the separations among the 2.138, 2.256, 2.364, and 2.468 eV peaks are similar and could be due to a vibrational progression. Two more similar vibrational progressions were observed at higher binding energies [(E) and (F)]. These progressions were assigned to be from the detachment of an electron from the 2σ orbital, based on their similarity. The broad vibrational progressions and their reduced vibrational frequencies were consistent with the removal of a bonding electron. Therefore, we assigned the 2.138 eV peak to be the 0–0 transition of a broad vibrational progression due to the $C^5\Sigma^-$ state derived from removal of a 2σ electron [Eq. (3)]. The strong 2.256 eV peak then must contain two components, one from the 0→1 transition of the $C^5\Sigma^-$ state and another electronic state which was the dominating one. In the above we assigned the latter to be due to the $^1\Delta$ state, derived from removing a 1δ electron [Eq. (2)].

Among all the states derived from removing a 2σ electron, the $^5\Sigma^-$ state was expected to have the lowest energy, followed by a set of triplet states and then the singlet states. Due to the strong bonding nature of the 2σ orbital, all of the electronic states derived from removing an electron from this orbital were expected to have broad and similar vibrational progressions with frequencies lower than that of the ground state. The observation and assignment of the three vibrational progressions [(C), (E), and (F)] were consistent with this expectation. However, the ordering of the triplet states were not known *a priori*. Among all the triplet states, the $^3\Gamma$ state was expected to give a complicated spectrum due to its spin-orbit splitting. Therefore, we tentatively assigned the

TABLE III. Comparison of the experimental spectroscopic constants of MoC to theoretical calculations.^a

States	Term value (cm ⁻¹)		Vib. freq. (cm ⁻¹)	
	Exp.	Theo	Exp.	Theo
$X^3\Sigma^-$	0	0	1000 (100)	997
$A^3\Delta$	4120 (200) ^b	4500		
$B^1\Gamma$	5750(160)	7207		
$C^5\Sigma^-$	6290 (80)	6178	890 (60)	891
$D^1\Delta$	7250 (80)	9312	[890 (60)]	1026

^aReference 14.

^bAverage over the three spin-orbit components.

(E) and (F) progressions to the two $^3\Sigma^-$ states, respectively. The peak at 3.40 eV was assigned to the $^3\Sigma^+$ state, also derived from the removal of the 2σ electron. A similar vibrational progression was expected for this state and the higher vibrational levels were beyond the 355 nm photon energy.

The observed binding energies of all the spectral features are given in Table I, as well as the derived term values and vibrational frequencies. The low-lying electronic states of MoC have been calculated at fairly high level by Shim and Gingerich,¹⁴ who took into account the relativistic effects expected to be important for MoC. The calculated term values and vibrational frequencies are compared to the current experiment in Table III. The calculated term values are in good agreement with the experiment, lending some credence for the spectral assignments.

B. WC

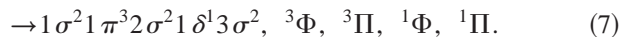
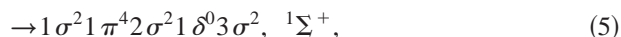
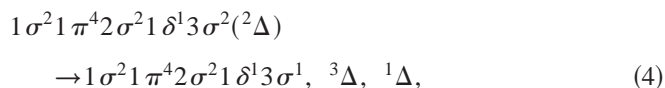
As we mentioned above, there is no theoretical calculation on WC. However, we can gain a qualitative understanding of the bonding in WC based on that in MoC. As we move down the periodic table from $4d$ to $5d$, the $6s$ orbital is stabilized relative to the $5d$ due to the strong relativistic effects. Thus, W has a $5d^46s^2$ ground state configuration, in contrast to $4d^55s^1$ for Mo. We can expect that this difference in the atomic configurations between W and Mo to be reflected in WC and MoC. To form chemical bonding to C, a $6s$ electron in W is expected to be promoted to the $5d$ orbital. The promotion energy is only 0.366 eV.¹⁵ Therefore, the MO picture shown in Fig. 3 for MoC should be qualitatively correct for WC (by replacing $4d$ and $5s$ with $5d$ and $6s$), except that the ordering or spacing between the 1δ and 3σ MOs is expected to be different. In WC, the 3σ orbital is either lower in energy than the 1δ or very close in energy with the 1δ . Therefore, the ground state configuration of WC could be either $3\sigma^2$ or $1\delta^13\sigma^1$. The $3\sigma^2$ configuration would give a $^1\Sigma^+$ ground state for WC whereas the $1\delta^13\sigma^1$ configuration would mean a $^3\Delta$ ground state for WC.

The 532 nm PES spectrum of WC⁻ shown in Fig. 2 should reveal the ground state of WC. Five well resolved peaks were observed, among which the lowest binding energy peak (X') was either due to an excited state of WC⁻ or a hot band transition because its relative intensity was always very weak and could be slightly changed under different experimental conditions. The remaining four peaks show a

rather complicated spectral pattern with various spacings and cannot be assigned to a single vibrational progression. If we assume the ground state of WC to be $3\sigma^2$, WC^- should have a $3\sigma^2 1\delta^1$ ground state configuration. In the PES spectrum, we would expect a strong ground state feature due to removal of the 1δ electron, followed by two features ($^3\Delta$ and $^1\Delta$) due to removal of a 3σ electron. The $^3\Delta$ state should also contain three spin-orbit components. If we assign the strong peak at 1.174 eV to the ground state transition, we would not have the expected spectral pattern due to the $^3\Delta$ and $^1\Delta$.

Alternatively, if we assume the ground state of WC to be $1\delta^1 3\sigma^1$ ($^3\Delta$), the WC^- ground state could be $1\delta^1 3\sigma^2$ ($^2\Delta$). In the PES spectrum, this anion configuration would give a $^3\Delta$ and a $^1\Delta$ state due to removal of a 3σ electron and a strong peak due to removal of the 1δ electron. Our observed PES spectrum at 532 nm could be satisfactorily assigned with these transitions, as shown in Fig. 2. The strong peak ($A^1\Sigma^+$) due to the removal of the 1δ electron overlapped with one of the spin-orbit components of the $^3\Delta$ ground state. The close separation between the $X^3\Delta$ ground state and the $A^1\Sigma^+$ excited state is understandable because the 3σ and 1δ orbitals were expected to be nearly degenerate. This assignment yields an adiabatic EA of 1.022 eV for WC.

The overall detachment transitions from the top few MOs of WC^- are shown below:



With the $1\delta^1 3\sigma^2$ ($^2\Delta$) ground state configuration of WC^- , only singlet and triplet excited states of WC are accessible. Detachment channels [Eqs. (4) and (5)] were observed at 532 nm. The other higher energy channels should be observed at 355 nm. The next detachment channel [Eq. (6)] involves the removal of a 2σ electron, giving rise to a $^3\Delta$ and $^1\Delta$ state. The $^3\Delta$ state was expected to exhibit a pattern of spin-orbit splitting. The first features in the 355 nm spectrum beyond those observed at 532 nm were the group of weak features between 2.5 and 2.8 eV, which we tentatively assigned to the $C^3\Delta$ state due to the removal of a 2σ electron. The strong peak at 3.071 eV was assigned to the $D^1\Delta$ state derived from the same configuration [Eq. (6)]. Similar to the MoC spectrum, we again observed that the $^1\Delta$ transition seemed to have much higher intensity than the $^3\Delta$ state.

The remaining spectral features in the 355 nm spectrum again showed a group of three weak features between 3.2 and 3.4 eV and a strong peak at 3.426 eV. As shown in Fig. 2, we tentatively assigned the three features to the $^3\Phi$ state due to the removal of a 1π electron [Eq. (7)]. Three spin-orbit components were expected for this state and were consistent with the observed spectral pattern. The sharp peak at 3.426 eV was then assigned to the $^3\Pi$ state from the same configuration. There should also be spin-orbit components for the $3P$ state at higher binding energies beyond the cur-

rent spectral range. All of our assignments were shown in Fig. 2 and the binding energies and spectroscopic constants of all the observed features are listed in Table II.

Due to the lack of any previous work on WC, we again emphasize that the current assignments are tentative. However, the singlet and triplet spectral patterns and the spin-orbit splitting anticipated for the triplet states were born out fairly well in the PES spectra, thus lending some credence to the deduction of the MO configurations in WC and WC^- and to the spectral assignments. The electron affinity of WC (1.022 eV) was observed to be lower than that of MoC (1.358 eV), in contrast to the atoms, where W has a slightly higher EA than Mo.¹⁷ This is likely due to the electron-electron repulsion in the 3σ orbital in WC^- , where there are two electrons in the 3σ orbital, whereas there is only one electron in the 3σ orbital in MoC^- . The current spectral assignments will need confirmation from further theoretical studies, which will also be important to provide a quantitative understanding of the chemical bonding in WC.

IV. CONCLUSIONS

We reported the first photoelectron spectra of MoC^- and WC^- at two photon energies, 532 and 355 nm. The PES spectra provided both the electron affinities of MoC and WC and a wealth of low-lying excited states for the two neutral diatomics. For MoC, we observed seven low-lying excited states within ~ 2 eV of the ground state and compared these observations with available theoretical calculations. Our PES study provided the first spectroscopic information on WC. We observed six low-lying excited states for WC within 2.4 eV above its ground state. The bonding and molecular orbitals of WC were discussed and compared to that of MoC. We tentatively deduced that the bonding and spectroscopy of MoC and WC are different due to their different atomic configurations. The electron affinity of WC was observed to be lower than that of MoC.

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