



Anion photoelectron spectroscopy of TaO_n^- ($n = 1-3$)

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ABSTRACT

Negative ion photoelectron spectra of TaO_n^- , $n = 1-3$ are reported. By comparing this data to previous theoretical and experimental studies, the photodetachment transitions in the spectra of TaO^- and TaO_2^- were assigned. As a result, the adiabatic electron affinities of TaO and TaO_2 were determined to be 1.07 ± 0.06 eV and 2.40 ± 0.06 eV, respectively. Additionally, the dissociation energy of the TaO^- anion was determined to be 7.91 ± 0.19 eV. Similarities and dissimilarities of TaO^- vs. VO^- , TaO_2^- vs. VO_2^- , and TaO_3^- vs. VO_3^- are discussed.

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1. Introduction

Transition metal oxides are of technological and fundamental interest in fields as diverse as catalysis, microelectronics, and astrophysics. A knowledge of the electronic structures of transition metal oxides is fundamental to understanding many of the phenomena associated with these topics. While the role of d-electrons complicates the electronic structure of all of the transition metals and their oxides, this is especially so in the case of the heavy (third row) transition metal oxides. Anion photoelectron spectroscopy provides insight into their electronic structures. This technique provides not only electron affinities, but also information about the electronic and vibrational states of the anion's neutral counterpart. When supported by calculations, additional information about electronic and geometric structure can also be inferred. Our group has used this technique to study both transition and non-transition metal oxides and their anions [1–7].

Tantalum oxides have attracted substantial attention because of their importance in high-temperature chemistry and their occurrence in stellar atmospheres [8]. The optical spectrum of TaO has been reported in gas phase [9] and in inert gas matrices [10]. The electronic ground state of TaO is $^2\Delta$, with the $X^2\Delta_{5/2}$ spin component lying at 3505 cm^{-1} (0.4346 eV) above the $X^2\Delta_{3/2}$ spin component. The emission spectrum of TaO has been further investigated by Ram and Bernath [11,12] and Al-Khalili et al. [13]. Also, the dissociation and ionization energies have been determined for TaO and TaO_2 by mass spectrometric and photoelectron spectroscopic experiments [14–16]. In addition, using matrix-isolation infrared spectroscopy combined with calculations, the structures, and vibrational spectra of TaO, TaO^+ , TaO_2 , TaO_2^+ , TaO_2^- , TaO_3 , and TaO_3^- were studied [17,18].

Using density functional theory, Wu et al. [19] calculated ground state geometries and vibrational frequencies of TaO_n , $n = 1-3$ molecules in their neutral, positive, and negative charge states. They also computed electron affinities (EAs), ionization potentials, and dissociation energies for their neutral forms. In addition, calculations have been conducted on the low-lying, excited electronic states of neutral TaO_n , $n = 1-3$ [19–22]. For example, Wu et al. [19] reported that the $^4\Sigma^+$ state lies 0.46 eV above the ground state of TaO, and Dolg et al. [22] calculated that the $^4\Sigma^-$ state is 0.76 eV above the ground state of TaO.

In the present work, we report the negative ion photoelectron spectroscopic study of TaO_n^- , $n = 1-3$. We have assigned the observed photodetachment transitions in the photoelectron spectra of TaO^- and TaO_2^- , and we have determined the adiabatic electron affinity values for TaO and TaO_2 .

2. Experimental

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected anion beam with a fixed frequency laser beam and energy-analyzing the resultant photodetached electrons. Photodetachment is governed by the energy-conserving relationship,

$$h\nu = \text{EKE} + \text{EBE} \quad (1)$$

where $h\nu$ is the photon energy, EKE is the measured electron kinetic energy, and EBE is the electron binding (photodetachment transition) energy.

Our anion photoelectron spectrometer consists of a laser vaporization source, a linear time-of-flight mass spectrometer, a photodetachment laser, and a magnetic bottle electron energy analyzer. The laser vaporization source utilized second harmonic light pulses from a Nd:YAG laser (532 nm, 2.33 eV/photon). The photodetachment laser employed third harmonic light pulses from another Nd:YAG laser (355 nm, 3.49 eV/photon). The resolution of our magnetic bottle electron energy analyzer is ~ 35 meV at EKE of ~ 1 eV.

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Our apparatus has been described in detail elsewhere [23]. In these experiments, our photoelectron spectra were calibrated against the well known spectrum of Cu^- .

Metal oxide anions were generated in the laser vaporization source by focusing light pulses from its laser onto a tantalum foil wrapped metal rod (6 mm diameter). The target rod was continuously rotated and translated by a motor so that the laser would strike a fresh sample surface each time it was fired. Highly purified helium was used as the carrier gas, and injected into the ion source through a pulsed valve having a 4 atm backing pressure. Even so, there was enough oxygen present in the gas or on the sample surface to produce the desired anions without adding additional oxygen.

3. Results

The photoelectron spectra of TaO_n^- , $n = 1-3$ are presented in Fig. 1, along with the photoelectron spectrum of atomic Ta^- which is

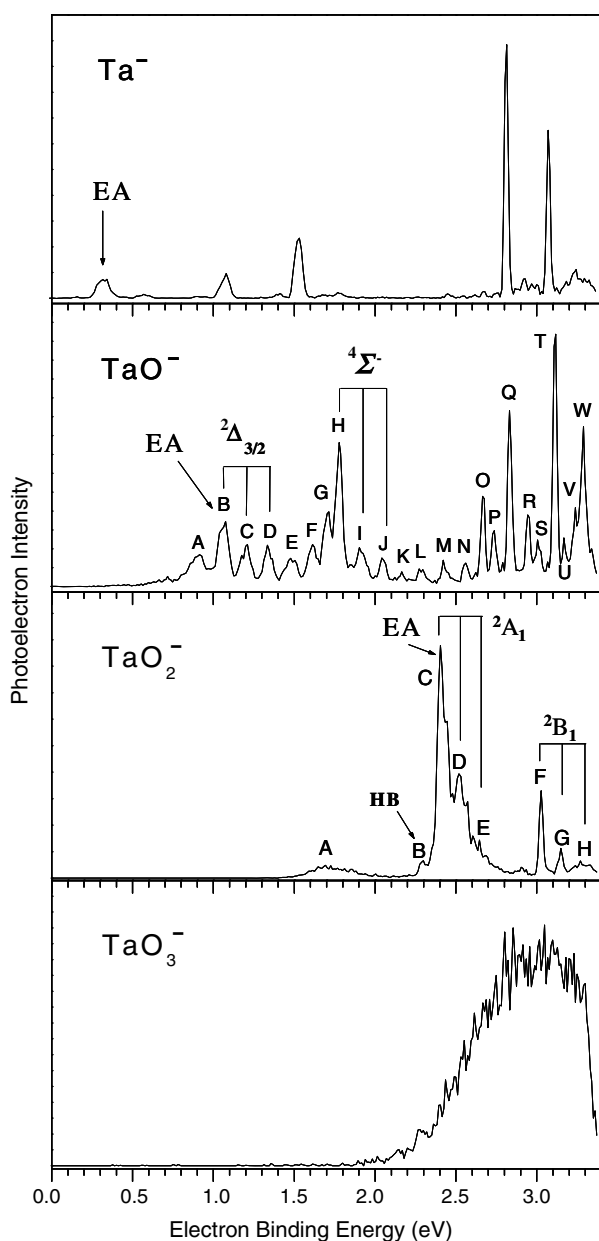


Fig. 1. Anion photoelectron spectra of TaO_n^- , $n = 0-3$ recorded using 355 nm (3.49 eV). The origin transitions are marked as EA.

shown for comparison. Our measured electron affinity of Ta is 0.32 ± 0.06 eV. This is consistent with the previously measured value of 0.323 ± 0.012 eV [24]. The photoelectron spectrum of TaO^- is highly structured with the peaks labeled as B, H, O, Q, T, and W being particularly prominent. In the photoelectron spectrum of TaO_2^- , three main spectral regions are observed: those comprising peak A, peaks B–E, and peaks F–H. The spectrum of TaO_3^- exhibits a single broad band at high electron binding energy. The four photoelectron spectra shown in Fig. 1 are dramatically different.

4. Discussion

4.1. TaO and TaO^-

As derived from its $\sigma^2\delta^1$ valence electronic configuration and based on previous spectroscopic studies, neutral TaO is thought to have a ${}^2\Delta$ ground electronic state [10]. This state is itself split into ${}^2\Delta_{5/2}$ and ${}^2\Delta_{3/2}$ spin-orbit components with the former sitting 3505 cm^{-1} (0.43 eV) above the latter [9]. In addition, theoretical studies on low-lying excited states of TaO found the ${}^4\Sigma^+$ and the ${}^4\Sigma^-$ states to lie 0.46 eV and 0.76 eV above the ground state, respectively [19–22]. Several higher energy states of TaO, e.g., $A''^2\Delta_{3/2}$, $A'^2\Pi_{1/2}$, $B^2\Phi_{5/2}$, $C^2\Pi_{3/2}$, and $C'^2\Delta_{3/2}$, have also been assigned from emission spectra [13]. The TaO^- anion with a $\sigma^2\delta^2$ electronic configuration has a ${}^3\Sigma^-$ ground state according to the calculations [19]. The expected nonbonding character of the excess electron in TaO^- was confirmed theoretically; the bond lengths of TaO and TaO^- were calculated to be 1.691 Å and 1.741 Å, respectively [19].

The electron binding energies and term energies of the peaks (photodetachment transitions) observed in the photoelectron spectrum of TaO^- along with our assignments are presented in Table 1. We assign peak B to the $X^3\Sigma^-(v''=0) \rightarrow X^2\Delta_{3/2}(v'=0)$ transition, i.e., the origin transition from the ground vibronic state of the TaO^- anion to the ground vibronic state of the TaO neutral. Peak E is assigned to the $X^3\Sigma^-(v''=0) \rightarrow {}^2\Delta_{5/2}$ and ${}^4\Sigma^+(v'=0)$ transitions, which are closely spaced. We assign peak H to the $X^3\Sigma^-(v''=0) \rightarrow {}^4\Sigma^-(v'=0)$ transition. Among the higher EBE peaks, we assign peaks M, O, P, and S to transitions from the $X^3\Sigma^-$ state of TaO^- to the $A''^2\Delta_{3/2}$ and $A'^2\Pi_{1/2}$ state, the $B^2\Phi_{5/2}$ state, the $C^2\Pi_{3/2}$ state, and the $C'^2\Delta_{3/2}$ states of TaO, respectively. We further assign peaks C and D as the $X^3\Sigma^-(v''=0) \rightarrow X^2\Delta_{3/2}(v'=1$ and $2)$ transitions, respectively. The spacings between peaks B–C and C–D are each 0.13 eV which is very close to the vibrational frequency for the ${}^2\Delta_{3/2}$ ground state of TaO, 1029 cm^{-1} (0.128 eV) [25]. We also assign peaks I and J as the $X^3\Sigma^-(v''=0) \rightarrow {}^4\Sigma^-(v'=1$ and $2)$ transitions. The spacings between peaks H–I and I–J are again 0.13 eV, in close agreement with the calculated vibrational frequency for the ${}^4\Sigma^-$ state of TaO, 1003 cm^{-1} (0.124 eV). These two sets of transitions are vibrational progressions.

Since peak B is the origin peak, the adiabatic electron affinity (EA) of TaO is 1.07 ± 0.06 eV. This value is in good agreement with the calculated value of 0.998 eV [19]. We do not believe peak A to be the origin peak. We reached this conclusion based on two pieces of evidence. First, peak A is spaced 0.16 eV from peak B, larger than the 0.13 eV spacings between peaks B–C and C–D. Second, it is not consistent with Franck–Condon simulations of the operative portion of the spectrum. When we conducted Franck–Condon simulations over the peak A through peak D region of the spectrum, using the known bond length and vibrational frequency of TaO [11,12] and values at and near the calculated vibrational frequency of TaO^- (919 cm^{-1}) as inputs [19], we could not fit this portion of the spectrum regardless of temperature. In addition, the intensity of peak A did not change with different source conditions. Thus, peak A does not appear to be a vibrational hot band. If it were, the peak A–B spacing should be less than 0.13 eV and the intensity of peak A

Table 1
The electron binding energies (EBEs), term energies and our assignments of TaO states (uncertainty ± 0.06 eV)

| Peak | EBE (eV) | T_e (eV) | Assignment $X^3\Sigma^- (v'' = 0) \rightarrow$ | Peak | EBE (eV) | T_e (eV) | Assignment $X^3\Sigma^- (v'' = 0) \rightarrow$ |
|------|----------|------------|--|------|----------|------------|--|
| A | 0.90 | -0.16 | | M | 2.42 | 1.35 | $A''^2\Delta_{3/2}, A'^2\Pi_{1/2}$ |
| B | 1.07 | 0 | $X^2\Delta_{3/2} (v' = 0)$ | N | 2.56 | 1.49 | |
| C | 1.20 | 0.13 | $X^2\Delta_{3/2} (v' = 1)$ | O | 2.66 | 1.59 | $B^2\Phi_{5/2}$ |
| D | 1.33 | 0.26 | $X^2\Delta_{3/2} (v' = 2)$ | P | 2.74 | 1.67 | $C^2\Pi_{3/2}$ |
| E | 1.49 | 0.42 | $^2\Delta_{5/2}, ^4\Sigma^+$ | Q | 2.83 | 1.76 | |
| F | 1.61 | 0.54 | | R | 2.94 | 1.87 | |
| G | 1.71 | 0.64 | | S | 3.01 | 1.94 | $C^2\Delta_{3/2}$ |
| H | 1.78 | 0.71 | $^4\Sigma^- (v' = 0)$ | T | 3.11 | 2.04 | |
| I | 1.91 | 0.84 | $^4\Sigma^- (v' = 1)$ | U | 3.17 | 2.10 | |
| J | 2.04 | 0.97 | $^4\Sigma^- (v' = 2)$ | V | 3.24 | 2.17 | |
| K | 2.17 | 1.10 | | W | 3.29 | 2.22 | |
| L | 2.28 | 1.21 | | | | | |

should vary with source conditions. However, when we next performed a Franck–Condon simulation over only the peak B through peak D region, we obtained a good fit. Furthermore, this simulation implied a bond length for TaO⁻ of 1.773 Å, reasonably close to the calculated bond length for TaO⁻ of 1.741 Å [19]. Together, these analyses corroborated the assignment of peak B as the origin peak and suggested that peak A is likely due to the photodetachment transition from an excited electronic state of the TaO⁻ anion to the ground electronic state of TaO, i.e., the energy of the first excited state of TaO⁻ is 0.16 eV above the ground $^3\Sigma^-$ state of the TaO⁻ anion.

In addition, the dissociation energy of the TaO⁻ anion into Ta and O⁻, i.e., $D_0(\text{Ta-O}^-)$, can be extracted from the data by utilizing the identity,

$$D_0(\text{Ta-O}^-) = D_0(\text{Ta-O}) + \text{EA}(\text{TaO}) - \text{EA}(\text{O}) \quad (2)$$

where $\text{EA}(\text{TaO}) = 1.07 \pm 0.06$ eV, $\text{EA}(\text{O}) = 1.461$ eV [26], and the dissociation energy of neutral TaO, $D_0(\text{Ta-O}) = 8.30 \pm 0.13$ eV [16]. Thus, $D_0(\text{Ta-O}^-) = 7.91 \pm 0.19$ eV, only 0.39 eV lower in energy than $D_0(\text{Ta-O})$. While the calculation of Wu et al. [19] under-estimated the value of $D_0(\text{Ta-O}^-)$, it is consistent with the result that $D_0(\text{Ta-O}^-) < D_0(\text{Ta-O})$. The close values of the dissociation energies of TaO and TaO⁻ are consistent with the excess electron in TaO⁻ residing in a nonbonding orbital and with most of the excess electron density residing on the oxygen atom in TaO⁻.

4.2. TaO₂ and TaO₂⁻

Relatively little information is available about TaO₂ and TaO₂⁻ from the experimental literature. However, recent calculations by Wu et al. have provided significant insight into the nature of both species [19]. These calculations found the ground state of TaO₂ to be 2A_1 . The bond distances between the Ta and O atoms in C_{2v} TaO₂ were found to be 1.729 Å, and the $\angle\text{O-Ta-O}$ was found to be 106.0°. The ground state of the TaO₂⁻ anion was determined to be a 1A_1 state. The Ta–O bond lengths in C_{2v} TaO₂⁻ were found to be 1.757 Å with a $\angle\text{O-Ta-O}$ angle of 109.4°, both of which are only slightly larger than the analogous parameters in the TaO₂ neutral. The EA of TaO₂ was calculated to be 2.200 eV.

As mentioned above, there are three main spectral regions observed in the photoelectron spectrum of TaO₂⁻: those including peak A, peaks B–E, and peaks F–H. Peak A is a broad band centered at 1.70 eV. Among the second group of peaks, peaks B, C, D, and E are centered at 2.30 eV, 2.40 eV, 2.52 eV, and 2.64 eV, respectively, with peak C having the strongest intensity. Among the third group, peak F is located at 3.03 eV, with peaks G and H at 3.15 eV and 3.27 eV, respectively. The EBEs, term energies and our assignments of the transitions in the photoelectron spectrum of TaO₂⁻ are presented in Table 2.

Table 2
The electron binding energies (EBEs), term energies and our assignments of TaO₂ states

| Peak | EBE (eV) | T_e (eV) | Assignment |
|------|----------|------------|--|
| A | 1.70 | -0.70 | $a^3B_2 (v'' = 0) \rightarrow X^2A_1 (v' = 0)$ |
| B | 2.30 | -0.10 | $X^1A_1 (v'' = 1) \rightarrow X^2A_1 (v' = 0)$ |
| C | 2.40 | 0 | $X^1A_1 (v'' = 0) \rightarrow X^2A_1 (v' = 0)$ |
| D | 2.52 | 0.12 | $X^1A_1 (v'' = 0) \rightarrow X^2A_1 (v' = 1)$ |
| E | 2.64 | 0.24 | $X^1A_1 (v'' = 0) \rightarrow X^2A_1 (v' = 2)$ |
| F | 3.03 | 0.63 | $X^1A_1 (v'' = 0) \rightarrow A^2B_1 (v' = 0)$ |
| G | 3.15 | 0.75 | $X^1A_1 (v'' = 0) \rightarrow A^2B_1 (v' = 1)$ |
| H | 3.27 | 0.87 | $X^1A_1 (v'' = 0) \rightarrow A^2B_1 (v' = 2)$ |

The photoelectron spectrum of TaO₂⁻ is similar to that of its congener, VO₂⁻ which was reported previously by Wang et al. [27]. There, in the comparable 3.49 eV photon energy window, two main transitions were observed in the photoelectron spectrum of VO₂⁻, these terminating on the X^2A_1 and the A^2B_1 states of neutral VO₂. Based on the combination of theoretical results and the experimental similarity between the photoelectron spectra of TaO₂⁻ and VO₂⁻, we assign peak C to the $X^1A_1 (v'' = 0) \rightarrow X^2A_1 (v' = 0)$ transition, i.e., the origin transition from the ground vibronic state of the TaO₂⁻ anion to the ground vibronic state of the TaO₂ neutral. This assignment leads to a determination of the EA of TaO₂ to be 2.40 ± 0.06 eV, a value which agrees well with the result predicted by theory [19]. Peaks D and E are assigned as $X^1A_1 (v'' = 0) \rightarrow X^2A_1 (v' = 1 \text{ and } 2)$ transitions. The spacings between peaks C–D and D–E are both 0.12 eV (968 cm⁻¹), in good agreement with the calculated value of 977.8 cm⁻¹ for the symmetric stretching frequency (ν_1) of ground state TaO₂ [17]. The profile of this vibrational progression is similar to that seen for VO₂⁻ and consistent with the prediction that there is only a slight structural difference between TaO₂ and TaO₂⁻. Peak B is spaced 0.10 eV (807 cm⁻¹) to the low EBE side of peak C. We assign it as the $X^1A_1 (v'' = 1) \rightarrow X^2A_1 (v' = 0)$ transition, i.e., as a vibrational hot band (marked as HB in Fig. 1). This value for a vibrational stretching frequency of the TaO₂⁻ anion is consistent with the expectation that it should be smaller than its counterpart in neutral TaO₂.

We assign peak F to the $X^1A_1 (v'' = 0) \rightarrow A^2B_1 (v' = 0)$ transition, i.e., the transition from the ground vibronic state of the TaO₂⁻ anion to $v' = 0$ of the first excited electronic state of the TaO₂ neutral. Peaks G and H are assigned as $X^1A_1 (v'' = 0) \rightarrow A^2B_1 (v' = 1 \text{ and } 2)$ transitions. The spacings between peaks F–G and G–H are both 0.12 eV (968 cm⁻¹), just as they were in the lower EBE vibrational progression. The similarities of these two profiles and their vibrational spacings suggest that the ground and first excited states of TaO₂ are structurally similar to each other and to the ground state of TaO₂⁻.

Peak A is broad and without resolved vibrational structure. We assign peak A as the transition from the first electronically excited state of the TaO_2^- anion to the ground state of neutral TaO_2 , $a^3B_2 \rightarrow X^2A_1$. The spacing between peaks A and C is about 0.7 eV. This is the energy of the first electronically excited state of TaO_2^- above the ground state of TaO_2^- , and it is consistent with the calculated value of 0.80 eV reported for this splitting [19]. Transitions from electronically excited anions were also seen in the photoelectron spectrum of VO_2^- , but they were closer in energy to the origin transition of VO_2^- , and they were not broad like peak A.

4.3. TaO_3 and TaO_3^-

The photoelectron spectrum of TaO_3^- is a broad, unresolved band in our experimental energy window. Calculations have found the EA of TaO_3 to be 4.04 eV which is much higher than the spectral feature that we observe starting at $\text{EBE} \sim 2$ eV [19]. Also, the EA of VO_3 is 4.36 eV [27]. Since the TaO_3^- spectrum does not appear to be due to dissociative photodetachment (no obvious candidates), possibly we are seeing transitions from an electronically excited anion of TaO_3^- .

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