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Photoelectron spectroscopy of the molecular anions, ZrO^- , HfO^- , HfHO^- , and HfO_2H^-

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Negative ion photoelectron spectra of ZrO^- , HfO^- , HfHO^- , and HfO_2H^- are reported. Even though zirconium- and hafnium-containing molecules typically exhibit similar chemistries, the negative ion photoelectron spectral profiles of ZrO^- and HfO^- are dramatically different from one another. By comparing these data with relevant theoretical and experimental studies, as well as by using insights drawn from atomic spectra, spin-orbit interactions, and relativistic effects, the photodetachment transitions in the spectra of ZrO^- and HfO^- were assigned. As a result, the electron affinities of ZrO and HfO were determined to be 1.26 ± 0.05 eV and 0.60 ± 0.05 eV, respectively. The anion photoelectron spectra of HfHO^- and HfO_2H^- are similar to one another and their structural connectivities are likely to be H-Hf-O^- and O-Hf-OH^- , respectively. The electron affinities of HfHO and HfO_2H are 1.70 ± 0.05 eV and 1.73 ± 0.05 eV, respectively. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4704127>]

INTRODUCTION

Transition metal oxides are technologically important because of the roles they play in catalytic processes and in high temperature chemistry. While zirconium and hafnium are generally thought to have similar chemical properties, some of their oxides show dissimilarities. In particular, ZrO_2 and HfO_2 show significant differences,^{1,2} which our previous work had attributed to subtle differences in their electronic structures.³

In the present work, we focus on the molecules, ZrO , HfO , HfHO , and HfO_2H and their anions. ZrO has been the subject of many spectroscopic investigations.^{4–12} Based on both experiments and theoretical calculations,^{13,14} the ground state of ZrO is generally thought to be $^1\Sigma^+$, although some calculations¹⁵ found it to be $^3\Delta$. Kaledin *et al.*⁵ have provided copious information on the electronic states of ZrO via wavelength-resolved fluorescence excitation studies. In addition, thermochemical and thermodynamic properties of ZrO have also been reported.^{16,17} Furthermore, there have been two previous anion photoelectron studies of ZrO^- , with the more recent one suggesting that ZrO may mimic the chemistry of palladium.^{18–20}

HfO has also been the subject of both spectroscopic and theoretical studies, these as in the case of ZrO also suggesting that its ground state is $^1\Sigma^+$.^{6,11,21–23} Again, Kaledin *et al.*²¹ measured the term energies of its electronic states. In addition, the thermodynamic properties of HfO ,¹⁶ as well as the

lifetimes²⁴ and dipole moments²⁵ of some HfO excited states have also been studied.

Here, we report the anion photoelectron spectra of ZrO^- , HfO^- , HfHO^- , and HfO_2H^- . The photoelectron spectra of ZrO^- and HfO^- are quite different from each other, suggesting significantly different electronic structures between these two, same-group transition metal monoxides. Information on the neutral electronic states of ZrO ⁵ and HfO ²¹ was used to make assignments of our anion photoelectron spectra, and the electron affinities (EA) of ZrO and HfO were extracted from their respective anion photoelectron spectra. The anion photoelectron spectra of HfHO^- and HfO_2H^- show a strong similarity to one another. Electron affinity values for HfHO and HfO_2H , along with structural insights, are reported.

EXPERIMENTAL

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency laser beam and energy-analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EKE is the measured electron kinetic energy, and EBE is the electron binding energy, i.e., the anion-to-neutral transition energy. These experiment were conducted on an apparatus consisting of a Nd:YAG laser vaporization source, a linear time-of-flight mass spectrometer, a mass gate, a momentum decelerator, a second Nd:YAG laser (for photodetachment), and a magnetic bottle electron energy analyzer. The resolution of our magnetic bottle electron

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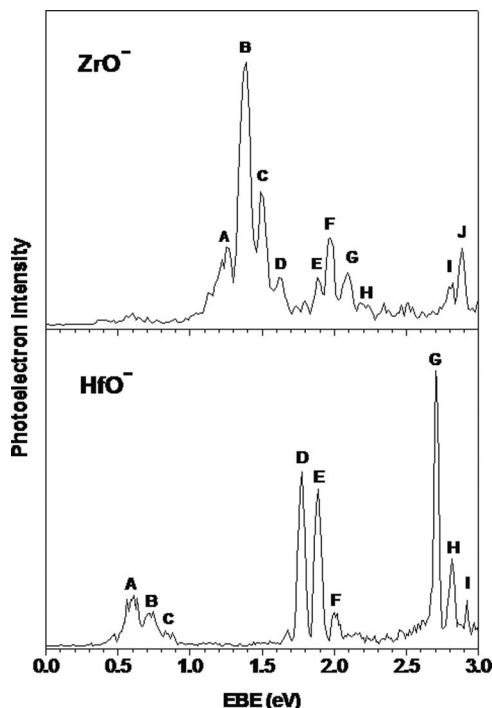


FIG. 1. Anion photoelectron spectra of ZrO^- and HfO^- recorded with 3.493 eV (355 nm) photons.

energy analyzer was ~ 35 meV at an EKE of ~ 1 eV. The apparatus has been described in detail in Ref. 26.

The anions, ZrO^- and HfO^- , were generated in a laser vaporization source by focusing the pulsed (10 Hz), second harmonic (532 nm) beam of a Nd:YAG laser onto a continuously rotating, translating zirconium or hafnium rod. The carrier gas used in the laser vaporization source was highly purified helium, which issued through a pulsed valve with a backing pressure of ~ 4 atm. The oxides on the surfaces of the zirconium and hafnium rods were found to be adequate for generating the metal oxide anions of interest without the addition of oxygen.

RESULTS

The anion photoelectron spectra of ZrO^- and HfO^- are shown in Figure 1, and those of HfHO^- and HfO_2H^- are pre-

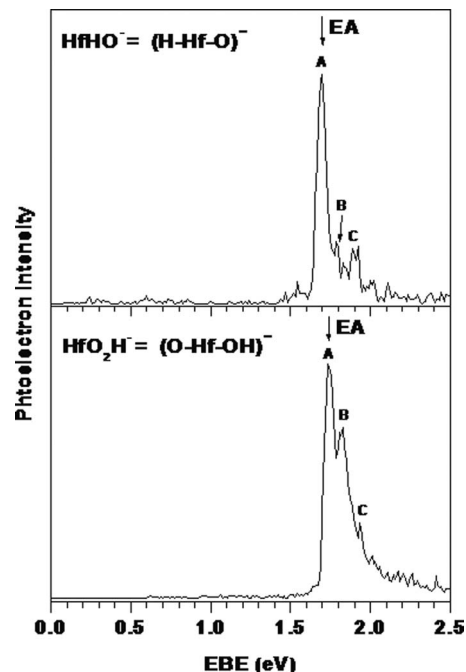


FIG. 2. Anion photoelectron spectra of HfHO^- and HfO_2H^- taken with 3.493 eV (355 nm) photons.

sented in Figure 2. All of these spectra were recorded with 3.49 eV photons. In all cases, the principal peaks in these spectra are labeled with capital letters; the EBE values of their centers are tabulated in Tables I–III (with uncertainties of ± 0.05 eV). The spectra of ZrO^- and HfO^- each exhibit three main groupings of peaks, with peak (B) at EBE = 1.39 eV dominating the spectrum of ZrO^- , and with peaks (D, E, G) at EBE = 1.78, 1.89, and 2.71 eV dominating the spectrum of HfO^- . The spectra of HfHO^- and HfO_2H^- show similar spectral profiles to one another, where in each case strong, relatively sharp peaks (labeled A in both cases) located at EBE = 1.70 and 1.73 eV, respectively, dominate their spectra.

DISCUSSION

ZrO^-

Our anion photoelectron spectrum of ZrO^- is consistent with the previously reported anion photoelectron spectra of

TABLE I. Transition assignments for the photoelectron spectrum of ZrO^- . T_e is the term energy in eV. (Uncertainty of EBE is ± 0.05 eV).

Peaks	EBE (eV)	T_e (eV)	Peak assignment: ${}^2\Delta \rightarrow$	ω_e (cm^{-1})
A	1.26	0	$X^1\Sigma^+ (v' = 0, 5s^2, \sigma\delta^2)$...
B	1.39	0.13	$A^3\Delta_1 (v' = 0, 4d^1 5s^1, \sigma^2\delta)$ and $X^1\Sigma^+ (v' = 1)$	890
C	1.50	0.24	$A^3\Delta_1 (v' = 1)$ and ${}^3\Delta_2 (4d^1 5s^1, \sigma^2\delta)$...
D	1.62	0.36	$A^3\Delta_1 (v' = 2)$ and ${}^3\Delta_3 (4d^1 5s^1, \sigma^2\delta)$...
E	1.88	0.62	$({}^2\Sigma^- \rightarrow {}^1\Delta_2)^a (4d^1 5s^1, \sigma^2\delta)$...
F	1.98	0.72	$A^1\Delta_2 (v' = 0, \sigma^2\delta)$	880
G	2.09	0.83	$A^1\Delta_2 (v' = 1)$ and ${}^3\Phi_2 (4d^2, \sigma^2\delta)$...
H	2.20	0.94	$A^1\Delta_2 (v' = 2)$ and ${}^3\Phi_3 (4d^2, \sigma^2\delta)$...
I	2.80	1.54	$b^3\Pi_0 (4d^2, \sigma^2\pi)$...
J	2.88	1.62	$b^3\Pi_1 (4d^2, \sigma^2\pi)$...

^aAssigned to a transition from an excited state of the anion to the neutral.

TABLE II. Transition assignments for the photoelectron spectrum of HfO^- . T_e is the term energy in eV, and ω_e is the measured vibrational frequency in cm^{-1} . (Uncertainty of EBE is ± 0.05 eV).

Peaks	EBE (eV)	T_e (eV)	Peak assignment: ${}^2\Delta \rightarrow$	ω_e (cm^{-1})
A	0.60	0	$X^1\Sigma^+$ ($v' = 0, 6s^2, \sigma\delta^2$)	1050
B	0.73	0.13	$X^1\Sigma^+$ ($v' = 1$)	
C	0.86	0.26	$X^1\Sigma^+$ ($v' = 2$)	
D	1.78	1.18	$a^3\Delta_2 + {}^1\Delta_2$ ($v' = 0, 5d^16s^1, \sigma^2\delta$)	890
E	1.89	1.29	$a^3\Delta_1$ ($v' = 0, 5d^16s^1, \sigma^2\delta$)	
F	2.00	1.40	$a^3\Delta_1$ ($v' = 1, 5d^16s^1, \sigma^2\delta$)	
G	2.71	2.11	$b^3\Pi_0$ ($v' = 0$) ($5d^2, \sigma^2\pi$)	890
H	2.82	2.22	$b^3\Pi_1 + {}^1\Pi_1$ ($v' = 0, 5d^2, \sigma^2\pi$)	
I	2.92	2.32	$b^3\Pi_2$ ($v' = 0, 5d^2$)	

ZrO^- ,^{19,20} although due to differences in resolution and photon energy windows, the present spectrum shows more spectral detail. We assign peak **A** at EBE = 1.26 eV as the origin transition in the photoelectron spectrum of ZrO^- , i.e., the transition from the ground vibrational ($v'' = 0$) and electronic (${}^2\Delta$) state of the ZrO^- anion to the ground vibrational ($v' = 0$) and electronic (${}^1\Sigma^+$) state of neutral ZrO . The ground state of anion was determined based on the fact that the relativistic mass-velocity stabilization of the $6s$ orbital of Zr would favor the σ orbital over the δ orbital of ZrO^- . It means that the ground state of HfO^- should have been arisen from the $\sigma^2\delta$ configuration (${}^2\Delta$) rather than $\sigma\delta^2$ (${}^2\Sigma^-$). This assignment determines the adiabatic EA of ZrO to be 1.26 eV, in agreement with previous experiments and calculations.^{14,15,18–20} Peak **A** is the lowest EBE peak which does not vary in intensity with source conditions relative to the other higher EBE peaks. The two slightly lower EBE, shoulder peaks at EBE ~ 1.1 and ~ 1.2 eV vary with source conditions and are likely to be due to the photodetachment of vibrationally excited ground state anions; they are vibrational hot bands. The low intensity signal in the EBE region between 0.3–0.7 eV was also seen in a previous study and was assigned as an electronic hot band, i.e., as being due to photodetachment transitions from an electronically excited anion.

With the EBE value of the origin transition established, the spectroscopic assignments of neutral ZrO by Kaledin *et al.*⁵ were used to assign the other significant transitions in the anion photoelectron spectrum of ZrO^- . These assignments are presented in Table I.^{5,36} The most intense feature in the spectrum is peak **B**, located at EBE = 1.39 eV. It and its associated vibronic peaks, **C** and **D**, correspond to transitions

TABLE III. Measured EA values of HHfO and OHfOH , and the measured vibrational frequency of OHfOH^- . (Uncertainty of EBE is ± 0.05 eV).

Systems	Peaks	EBE (eV)	ω_e (cm^{-1})
HHfO	A	1.70	730
	B	1.79	
	C	1.89	
OHfOH	A	1.73	810
	B	1.83	
	C	1.93	

from the ground state anion to the various components of the first excited ${}^3\Delta_1$ state of neutral ZrO . While the **B-C** and **C-D** spacings were measured to be 890 cm^{-1} , the vibrational frequency of the ${}^3\Delta_1$ state cannot be unambiguously determined from this spectrum, since the ${}^3\Delta_2$ spin-orbit component lies in the same region as the vibrational transitions to the ${}^3\Delta_1$ state, causing the features associated with both to overlap. Nevertheless, we expect the vibrational frequency of the ${}^3\Delta_1$ state to be very close to the spin-orbit splitting between ${}^3\Delta_1$ and ${}^3\Delta_2$ components. (Peak **E** is discussed and assigned below.) Similarly, peak **F**, located at EBE = 1.98 eV and its associated vibronic peaks, **G** and **H**, correspond to transitions from the ground state anion to the second excited state of neutral ZrO , ${}^1\Delta_2$. The peaks, **G** and **H**, are probably comprised of both transitions to vibrational levels of the ${}^1\Delta_2$ state and ${}^3\Phi_2$ and ${}^3\Phi_3$ spin-orbit components, which arise from the Zr^{2+} ($4d^2$) configuration. Based on the measured **F-G** and **G-H** spacings, the vibrational frequency of the ${}^1\Delta_2$ state is determined to be 880 cm^{-1} . Furthermore, peak **I**, located at EBE = 2.80 eV and peak **J**, located at EBE = 2.88 eV are, respectively, assigned to the transitions from the anion ground state to the ${}^3\Pi_0$ and ${}^3\Pi_1$ excited states of neutral ZrO . All of these assignments are presented in Table I.

In proposing these assignments, we have considered both prior assignments and an analysis of analogous electronic states for neutral ZrO . Due to the strong ionic nature of ZrO , we expect that the bonding can be described as being predominantly $\text{Zr}^{2+}\text{O}^{2-}$. Thus, the excited electronic states of ZrO can be analyzed and rationalized using the atomic energy levels of Zr^{2+} . Since the isoelectronic Y^+ atomic energy levels²⁷ are readily available, we have used the energy separations between Y^+ electronic states to provide additional guidance in the assignment of the observed photoelectron spectra of ZrO^- (see Figure 3). As seen from Moore's atomic spectra data,²⁷ the ground state of Y^+ is 1S with 3D_1 , 3D_2 , and 3D_3 excited states located at 840, 1045, and 1450 cm^{-1} ,

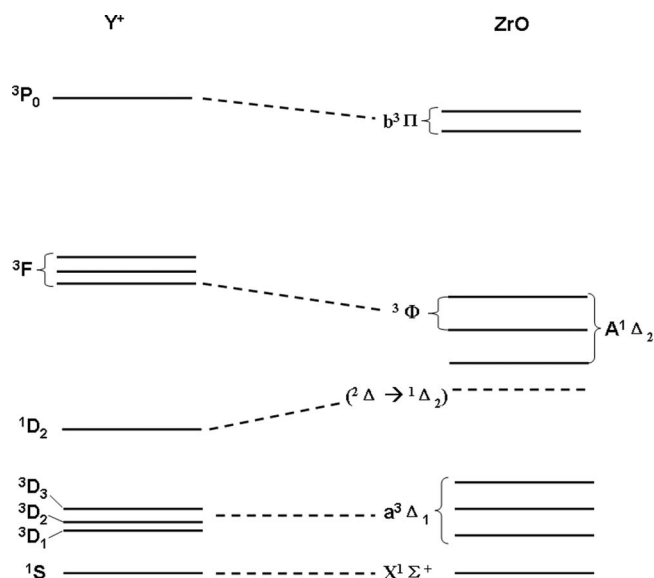


FIG. 3. Comparison between the atomic energy levels of Y^+ and the assigned molecular energy levels of neutral ZrO as extracted from the anion photoelectron spectrum of the ZrO^- anion.

respectively, above the ground state. These states could correspond to the observed transitions **B**, **C**, and **D** in the anion photoelectron spectrum of ZrO^- . Moreover, the $^1\text{D}_2$ excited state of Y^+ at 3296 cm^{-1} corresponds to the $^1\Delta_2$ excited state of neutral ZrO , which correlates with the $(4d^15s^1)$ configuration of Zr^{2+} . A transition from the $^2\Sigma^-$ electronically excited state of the ZrO^- anion to the $^1\Delta_2$ excited state of neutral ZrO can be assigned to peak **E**, which is an electronic hot band. In addition, the ^3F state of Y^+ , arising from the $4d^2$ configuration,³³ has a T_e of 8003 cm^{-1} , thereby supporting our assignment of peaks **G** and **H**, to the $^3\Phi_2$ and $^3\Phi_3$ spin-orbit components. Finally, the $^3\text{P}_0$ state of Y^+ is observed at $13\,883\text{ cm}^{-1}$, which supports our assignment of peak **I** to a transition terminating on the $^3\Pi_0$ excited state of neutral ZrO and our assignment of peak **J** to a transition terminating on the $^3\Pi_1$ excited state of neutral ZrO .

HfO⁻

We assign peak **A**, located at $\text{EBE} = 0.60\text{ eV}$ as the origin transition in the anion photoelectron spectrum of HfO^- , i.e., the transition from the ground vibrational ($v'' = 0$) and electronic ($^2\Delta$) state of the HfO^- anion to the ground vibrational ($v' = 0$) and electronic ($^1\Sigma^+$) state of neutral HfO . Similar to ZrO^- , the ground state of HfO^- anion was determined to have arisen from the $\sigma^2\delta$ configuration. This assignment determines the adiabatic EA of HfO to be 0.60 eV . Peak **A** is the lowest EBE peak, which does not vary in intensity with source conditions relative to the other higher EBE peaks. The intensity of the shoulder peak at slightly lower EBE (at 0.48 eV) varies with source conditions and is assigned as being due to the photodetachment of a vibrationally excited, ground electronic state anion; it is a vibrational hot band. Peaks **B** and **C** correspond, respectively, to transitions from the ground vibrational and electronic state of the HfO^- anion to the $v' = 1$ and the $v' = 2$ vibrational levels of the ground electronic state of neutral HfO . The **A-B** and **B-C** spacings were measured to be 1050 cm^{-1} , and this is a measure of the vibrational frequency of neutral HfO . This value is higher than the literature value,²¹ which is 967 cm^{-1} . We attribute this slight discrepancy to the low signal-to-noise ratio observed for this particular band. A Franck-Condon analysis of the band containing peaks **A**, **B**, **C** (using a program developed by Ervin and Lineberger²⁸) found the bond length of the HfO^- anion to be 1.759 \AA . The literature value of the neutral HfO bond length (and thus the input value utilized in the program) is 1.723 \AA . This difference is consistent with the expectation of a weaker bond and longer bond length for the HfO^- anion relative to its neutral HfO counterpart.

With the origin transition tentatively located, the spectroscopic assignments of neutral HfO by Kaledin *et al.*²¹ (see Ref. 36) were used to assign the other significant transitions in the anion photoelectron spectrum of HfO^- . The most intense features in the spectrum are peaks **D**, located at $\text{EBE} = 1.78\text{ eV}$, peak **E**, located at $\text{EBE} = 1.89\text{ eV}$, and peak **G**, located at $\text{EBE} = 2.71$. Relative to the EBE of peak **A**, peak **D** lies at an EBE which corresponds to a photodetachment transition from the ground state of the HfO^- anion to the $a^3\Delta_1$

excited state of neutral HfO , as assigned by Kaledin *et al.*²¹ Likewise, peak **E** lies at an EBE which corresponds to a transition to the similarly assigned $a^3\Delta_2$ excited state of neutral HfO . Peak **F** is a vibronic peak, corresponding to a transition from the ground state anion to $v' = 1$ of the $a^3\Delta_2$ state of neutral HfO . The **E-F** spacing, measured to be 890 cm^{-1} , is a measure of the vibrational frequency of the $a^3\Delta_2$ excited state of HfO . In similar fashion, peak **G** lies at an EBE which corresponds to a transition to the $b^3\Pi_0$ excited state of neutral HfO . Peaks **H** and **I** correspond to transitions to higher components of $b^3\Pi$ excited states of neutral HfO . The close correspondence between the energy levels of neutral HfO measured by Kaledin *et al.* and the peak locations in our observed spectrum confirms our assignment of the origin transition to peak **A**.

As was the case for ZrO above, we have also conducted an analysis of analogous electronic states for neutral HfO in order to further assist in making assignments. This approach involved utilizing the atomic energy levels²⁷ of La^+ . However, because there are lanthanide atoms between lanthanum and hafnium in the periodic table, we scaled the energies of the La^+ states by the atomic numbers of hafnium and lanthanum in order to make a meaningful comparison. The assignment of peak **A** as the origin transition remains unchanged. However, the assignments of peaks **D** and **E** differ slightly under this approach. Under the assignment based on Kaledin's work,²¹ peak **D** is due to a transition from the ground state of the HfO^- anion to the $a^3\Delta_1$ excited state of neutral HfO . Alternatively, peak **D** could be assigned to the $^2\Delta \rightarrow \Omega = 2$ ($^3\Delta_2 + ^1\Delta_2$) transition. Note that the mixing of $^3\Delta_2$ and $^1\Delta_2$ is expected to be substantial in hafnium due to its large spin-orbit interaction,^{29,30} and thus this state could be lowered in energy relative to the $\Omega = 1$ ($^3\Delta_1$) state. This argues for peak **E** being assigned to the $^2\Delta \rightarrow \Omega = 1$ ($^3\Delta_1$) transition. In other words, the Kaledin-based assignments of peaks **D** and **E** should perhaps be switched. In support of this possibility, we note that the corresponding states of La^+ violate Hund's rule in that the $^1\text{D}_2$ state of La^+ is lower than the spin-orbit components of the ^3D state due to the mixing of the $J = 2$ components of $^1\text{D}_2$ and $^3\text{D}_2$.³³ Thus, we tentatively assign peak **D** to a $\Omega = 2$ state, even though an assignment of peak **D** to $^3\Delta_1$ and of peak **E** to $\rightarrow \Omega = 2$ ($^3\Delta_2 + ^1\Delta_2$) cannot be ruled out. Peak **G** remains assigned to the $^2\Delta \rightarrow ^3\Pi_0$ transition. Peaks **H** and **I** may simply be transitions to vibrational levels of the $^3\Pi_0$ state. However, the other two spin-orbit components of the $^3\Pi$ state, namely, $\Omega = 1$ and $\Omega = 2$ states, can also be candidates for the assignments of peaks **H** and **I**. These assignments are presented in Table II.

Upon comparing the anion photoelectron spectra of ZrO^- and HfO^- , it is clear that these two systems show dramatically different spectral profiles. Such differences suggest that a single oxygen atom binding to these transition metals can induce significant changes in electronic properties, even though zirconium and hafnium are usually considered to be nearly chemically identical. More surprisingly, the difference between ZrO^- and HfO^- observed here is more substantial than that between ZrO_2^- and HfO_2^- .³ We suggest that these spectral differences between HfO and ZrO are due to much larger relativistic effects in hafnium than in zirconium, and indeed, relativistic effects are most dramatically manifested in

diatomic species.³¹ The relativistic mass-velocity effect stabilizes the $5s$ orbital of Zr and $6s$ orbital of Hf. The same effect destabilizes the $4d$ orbital of Zr and $5d$ orbital of Hf. Specifically, using HfO as an example, the σ orbital of HfO is expected to be relativistically stabilized by mass-velocity effect while the δ orbital of HfO is expected to be destabilized, due to the fact that its s orbital is composed of the $6s-5d^{**2}$ orbital of Hf, while the δ orbital is purely atomic Hf ($5d$). Indeed, the $^3\Delta$ state of HfO is placed 1.18 eV above the $^1\Sigma^+$ state, which evidently supports relativistic mass-velocity stabilization of the σ orbital of HfO and destabilization of the δ orbital of HfO. In addition, the relativistic mass-velocity stabilization of $6s$ and the destabilization of $5d$ is more pronounced for Hf, as it is heavier than Zr (the $^3\Delta$ state of ZrO is only 0.24 eV above the ground state of ZrO whereas for HfO, the corresponding lowest $^3\Delta$ spin-orbit component is 1.18 eV above the $^1\Sigma^+$ state).

The dissociation energies of the ZrO^- anion into Zr and O^- , $D_0(Zr-O^-)$, and of the HfO^- anion into Hf and O^- , $D_0(Hf-O^-)$, can be extracted from our data by utilizing the identity,

$$D_0(X-O^-) = D_0(X-O) + EA(XO) - EA(O), \quad (1)$$

where X is either Zr or Hf. Here, we determined that $EA(ZrO) = 1.26$ eV and that $EA(HfO) = 0.60$ eV, and $EA(O)$ is known to be 1.461 eV.³² Furthermore, the dissociation energies of neutral ZrO and HfO, i.e., $D_0(Zr-O)$ and $D_0(Hf-O)$, are 7.91 eV³⁰ and 8.19 eV,¹² respectively. Thus from these values, we can obtain the dissociation energy for their corresponding anions. The results are: $D_0(Zr-O^-) = 7.71$ eV and $D_0(Hf-O^-) = 7.33$ eV. Note that the value of $D_0(Zr-O^-)$ is very close to that of $D_0(Zr-O)$, i.e., only a difference of 0.20 eV. By comparison, the difference between $D_0(Hf-O^-)$ and $D_0(Hf-O)$ is much bigger, i.e., a difference of 0.86 eV.

HfHO⁻ and HfO₂H⁻

The anion photoelectron spectra of HfHO⁻ and HfO₂H⁻ are presented in Figure 2. These two spectra have very similar profiles, in which each displays a strong peak (labeled peak **A**) and two higher EBE transitions (labeled peaks **B** and **C**). All of these transitions are listed in Table III. In each case, we assign the peak **A** as the origin transition, this assignment determining the electron affinities of HfHO and HfO₂H to be 1.70 eV and 1.73 eV, respectively. We further assign peaks **B** and **C** in both cases as vibrational transitions associated with their corresponding peak **A**, i.e., transitions to $v' = 1$ and $v' = 2$, respectively. The **A-B** and **B-C** spacings in the spectrum of HfOH⁻ are essentially the same, at 730 cm⁻¹, while the **A-B** and **B-C** spacings in the spectrum of HfO₂H⁻ are the same, at 810 cm⁻¹. In both spectra, their relatively narrow spectral profiles and the curtailed extent of their vibrational progressions suggest that their anionic and neutral structures may be similar. Previous infrared and computational studies have shown that hafnium atoms can insert into O-H bonds to form HHfO.^{34,35} Thus, we propose that HfHO and HfHO⁻ exhibit the structural connectivity, H-Hf-O rather than

Hf-O-H and that HfO₂H and HfO₂H⁻ have the connectivity, O-Hf-O-H.

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