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Electronic Structure Differences in ZrO₂ vs HfO₂[†]

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Although ZrO₂ and HfO₂ are, for the most part, quite similar chemically, subtle differences in their electronic structures appear to be responsible for differing MO₂/Si (M = Zr, Hf) interface stabilities. To shed light on the electronic structure differences between ZrO₂ and HfO₂, we have conducted joint experimental and theoretical studies. Because molecular electron affinities are a sensitive probe of electronic structure, we have measured them by conducting photoelectron spectroscopic experiments on ZrO₂⁻ and HfO₂⁻. The adiabatic electron affinity of HfO₂ was determined to be 2.14 ± 0.03 eV, and that of ZrO₂ was determined to be 1.64 ± 0.03 eV. Concurrently, advanced electronic structure calculations were conducted to determine electron affinities, vibrational frequencies, and geometries of these systems. The calculated CCSD(T) electron affinities of HfO₂ and ZrO₂ were found to be 2.05 and 1.62 eV, respectively. The molecular results confirm earlier predictions from solid state calculations that HfO₂ is more ionic than ZrO₂. The excess electron in MO₂⁻ occupies an sd-type hybrid orbital localized on the M atom (M = Zr, Hf). The structural parameters of ZrO₂ and HfO₂ and their vibrational frequencies were found to be very similar. Upon the excess electron attachment, the M–O bond length increases by ca. 0.04 Å, the OMO angle increases by 2–4°, and frequencies of all vibrational modes become smaller, with the stretching modes being shifted by 30–50 cm⁻¹ and the bending mode by 15–25 cm⁻¹. Together, these studies unveil significant differences in the electronic structures of ZrO₂ and HfO₂ but not in their structural or vibrational characteristics.

Introduction

Zirconia (ZrO₂) and hafnia (HfO₂) are important materials due to their present and potential future applications in microelectronics,^{1–4} catalysis,^{5–7} and ceramics.^{8–11} Zirconium ([Kr]4d²5s²) and hafnium ([Xe]4f¹⁴5d²6s²) reside in the same group of the periodic table, with the most obvious electronic structure difference between them being that hafnium possesses a closed subshell of f-electrons and zirconium has no f-electrons. Also, as a result of ensuing lanthanide contraction,¹² both the atomic and the ionic radii of these atoms are nearly the same. As a result of these similarities, Cotton et al.¹² state “The chemistries of hafnium and zirconium are more nearly identical than for any other two congeneric elements.” Indeed, infrared spectra,¹³ microwave spectra,^{14,15} and theoretical calculations^{13–15} show that the vibrational frequencies of molecular ZrO₂ and HfO₂ are quite close in value, and their bond lengths and bond angles are very similar. This is a manifestation of the well-known chemical similarity of Zr and Hf, which is exemplified in their geochemistry: Hf is found in all zirconium minerals and the separation of the two elements is difficult.¹²

Nevertheless, in the solid state, differences emerge between ZrO₂ and HfO₂. For example, significant differences in elastic behavior and transition pressures were suggested for ZrO₂ and HfO₂,¹⁶ and the temperature-induced monoclinic to tetragonal transition is about 500 K higher in HfO₂ than in ZrO₂.¹⁷ Moreover, recent theoretical and experimental work¹⁸ found that the thermodynamic stabilities of ZrO₂ and HfO₂ films are quite different when they are in contact with silicon. In fact, of substantial practical interest, the same study indicates that the HfO₂/Si interface is stable with respect to silicide formation, whereas the ZrO₂/Si interface is not, making HfO₂ a contender as a replacement for SiO₂ as a high-*k* gate dielectric.¹⁸ Because thermodynamic stability is a critical property for microelectronic devices, it is important to better understand the source of the difference. Given that most structural properties of ZrO₂ and HfO₂ are very similar, differences between their solid state properties must trace back to subtle differences in electronic structure. The difference between adiabatic electron affinities of otherwise similar molecules provides a sensitive measure of their electronic structure differences. To determine these values experimentally, we measured the gas phase, anion photoelectron spectra of ZrO₂⁻ and HfO₂⁻, whereas to obtain them theoretically, we conducted electronic structure calculations on MO₂ and MO₂⁻ (M = Zr, Hf) using density functional theory (DFT) and wave function-theory-based ab initio methods.

Molecular ZrO₂ and HfO₂ were previously reported as polar structures.^{13–15,19} The results of a matrix isolation study indicated

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TABLE 1: Experimental Electron Affinities and Vibration Frequencies for TiO₂, ZrO₂, and HfO₂^a

	adiabatic electron affinity	vib freq from PES	vib freq from matrix IR ^b
TiO ₂	1.59 ± 0.03 eV ^c	940 ± 40 cm ⁻¹ (ν_1) ^c	946.9 cm ⁻¹ (ν_1), 917.1 cm ⁻¹ (ν_3)
ZrO ₂	1.64 ± 0.03 eV ^d	887 ± 40 cm ⁻¹ (ν_1) ^d	884.3 cm ⁻¹ (ν_1), 818.0 cm ⁻¹ (ν_3)
HfO ₂	2.14 ± 0.03 eV ^d	887 ± 40 cm ⁻¹ (ν_1) ^d	883.4 cm ⁻¹ (ν_1), 814.0 cm ⁻¹ (ν_3)

^a ν_1 symmetric stretching, ν_3 asymmetrical stretching, ν_2 bending, ν_2 is not shown here. ^b Reference 13. ^c Reference 38. ^d This PES experiment.

that the MO₂ (M = Zr, Hf) is bent, and the upper limit for $\angle\text{OMO}$ was assigned to $113 \pm 5^\circ$ and $115 \pm 5^\circ$ for M = Zr and Hf, respectively.¹³ The stretching frequencies of these C_{2v} structures are strikingly similar: $\nu_1(a_1) = 884.3$ and 883.4 cm⁻¹, $\nu_3(b_2) = 818$ and 814 cm⁻¹, for ZrO₂ and HfO₂, respectively; see also Table 1.¹³ More accurate structures were determined from rotational spectra: the Zr–O bond length is 1.7710 ± 0.0007 Å, $\angle\text{OZrO} = 108.11 \pm 0.08^\circ$,¹⁴ the Hf–O bond length is 1.7764 ± 0.0004 Å, $\angle\text{OHfO} = 107.51 \pm 0.01^\circ$.¹⁵ The electric dipole moments determined from Stark-effect measurements are 7.80 and 7.92 D for ZrO₂ and HfO₂, respectively.^{13,14} Finally, the frequency of the bending vibration of ZrO₂ was estimated to be 290 cm⁻¹, on the basis of its inertial defect.¹⁴

Methods

Experimental Methods. Anion 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. The technique is governed by the following 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 energy. The experiment was 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, and a magnetic bottle energy analyzer. The resolution of our magnetic bottle electron energy analyzer was ~ 35 meV at an EKE of ~ 1 eV. The apparatus has been described in the detail elsewhere.²⁰

The anions, ZrO₂⁻ and HfO₂⁻, were generated by a laser vaporization source by focusing the pulsed (10 Hz), second harmonic (532 nm) beam of a Nd:YAG laser onto a zirconium rod (6.2 mm diameter, 99%, Alfa AESAR #10443) in the former case and onto a hafnium rod (5.0 mm diameter, 97%, Goodfellow HF007910) in the latter case. In both cases, the target rod was continuously rotated and translated so that the laser struck a different spot each time it was fired. The carrier gas used in the laser vaporization source was highly purified helium, which issued through a pulsed valve, having a backing pressure of ~ 4 atm. Oxygen was not added to the carrier gas, because the oxygen on the surface of the zirconium and hafnium rods was found to be adequate for making the metal oxide anions of interest.

Franck–Condon analyses were conducted on both the ZrO₂/ZrO₂⁻ and the HfO₂/HfO₂⁻ systems using the PESCAL program.²¹

Theoretical Methods. Initial calculations were performed with relativistic SBKJ pseudopotentials and basis sets²² and the B3LYP exchange–correlation functional.²³ Advanced ab initio calculations were further carried out using the coupled cluster method with single, double, and noniterative triple excitations (CCSD(T)).²⁴ All electrons were treated on oxygens with aug-cc-pVTZ basis sets.²⁵ Stuttgart energy-consistent, small-core pseudopotentials and the (8s7p6d)/[6s5p3d] basis sets were used

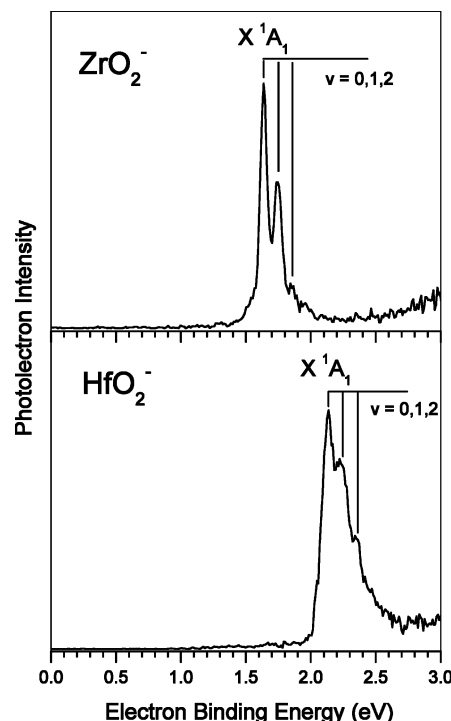


Figure 1. Photoelectron spectra of ZrO₂⁻ and HfO₂⁻ recorded with 3.493 eV photons.

for Zr and Hf.²⁶ As the excess electron in the anions are localized at the metal centers, the (8s7p6d)/[6s5p3d] basis sets of Zr and Hf were further expanded with polarization and diffuse functions as described below. A small basis set (denoted as S) on M (M = Zr, Hf) included a set of diffuse d functions $\zeta(M,d) = 0.01$ and a large basis set (denoted as L) included two f and one g polarization functions²⁷ and two diffuse s and two diffuse d functions. The exponents of s and d diffuse functions were obtained from even-tempered progressions with a constant of 0.5, initiated from the most diffuse s and d functions in the original (8s7p6d)/[6s5p3d] basis set. The scalar relativistic effects were taken into account via the relativistic pseudopotentials obtained from Wood–Boring all-electron calculations on the atoms.²⁶ Spin–orbit coupling effects might be important for the hafnium compounds but they were neglected in the current approach. The CCSD(T) forces and curvatures were calculated numerically. Excited electronic states of neutral ZrO₂ and HfO₂ were calculated using time-dependent density functional theory (TDDFT) with the L basis set and the B3LYP exchange–correlation functional. The DFT calculations were performed with Gaussian98²⁸ and CCSD(T) calculations with MOLPRO.²⁹ Molden was used for the visualization of singly occupied molecular orbitals.³⁰

Results

Experimental Results. The photoelectron spectra of ZrO₂⁻ and HfO₂⁻ are presented in Figure 1. They were both recorded with 3.493 eV photons, the third harmonic of Nd:YAG laser. Because Zr and Hf each have several isotopes, we recorded these

spectra on mass peaks, ⁹⁰ZrO₂⁻ and ¹⁷⁶HfO₂⁻ to avoid the possibility of contamination from nearby ZrO₂H⁻ and HfO₂H⁻. The electron binding energies (EBE) in both spectra were calibrated against the atomic lines of the copper anion, and the uncertainty of the calibration is ±0.03 eV. The spectrum of ZrO₂⁻ is consistent with our former low resolution result.³¹ The spectrum of ZrO₂⁻ exhibits a main peak at EBE = 1.64 eV, corresponding to the transition from *v* = 0 of the ground state of ZrO₂⁻ anion to *v* = 0 of the ground state of ZrO₂ neutral. This implies that the adiabatic electron affinity (AEA) of ZrO₂ is 1.64 ± 0.03 eV. The peaks at EBE = 1.75 and 1.86 eV correspond to excited vibrations (*v* = 1 and 2, respectively) in the electronic ground state of neutral ZrO₂. The energy spacings between adjacent peaks are both 0.11 ± 0.005 eV, corresponding to a vibrational frequency of 887 ± 40 cm⁻¹ for ZrO₂. This value is consistent with that of 884.3 cm⁻¹ obtained for the symmetrical stretching mode (*v*₁) of ZrO₂ in matrix infrared spectroscopy experiments;¹³ see Table 1. In analogous fashion, the photoelectron spectrum of HfO₂⁻ exhibits a main peak at EBE = 2.14 eV, corresponding to the transition from *v* = 0 of the ground state of HfO₂⁻ anion to *v* = 0 of the ground state of HfO₂ neutral. This implies that the AEA of HfO₂ is 2.14 ± 0.03 eV. The peaks at EBE = 2.25 and 2.36 eV correspond to excited vibrations (*v* = 1 and 2, respectively) in the electronic ground state of neutral HfO₂. Again, the energy spacings between adjacent peaks are both 0.11 ± 0.005 eV, corresponding to a vibrational frequency of 887 ± 40 cm⁻¹ for HfO₂. This value is also consistent with that of 883.4 cm⁻¹ obtained for the symmetrical stretching mode (*v*₁) of HfO₂ in matrix infrared spectroscopy experiments;¹³ see Table 1. We should mention that the uncertainties of *v*₁ frequencies obtained from the photoelectron spectra are larger than those from the matrix infrared spectra.¹³

Franck-Condon analyses were conducted on both the ZrO₂/ZrO₂⁻ and the HfO₂/HfO₂⁻ systems and the results fitted to their respective photoelectron spectra. For the ZrO₂⁻ photoelectron spectrum, our best fit was obtained when the symmetric stretch (*v*₁) of neutral ZrO₂ equaled 871 cm⁻¹ and when the AEA of ZrO₂ equaled 1.65 eV. Both of these values are consistent with our a priori assignment of the ZrO₂⁻ photoelectron spectrum. For the HfO₂⁻ photoelectron spectrum, our best fit was obtained when the symmetric stretch (*v*₁) of neutral HfO₂ equaled 872 cm⁻¹ and when the AEA of HfO₂ equaled 2.15 eV. Both of these values are again consistent with our a priori assignment of the HfO₂⁻ photoelectron spectrum. For both systems, the measured values of AEA and the *v*₁ frequencies are in excellent agreement with the calculated values, vide infra and Table 2.

Theoretical Results. The most stable structures of ZrO₂ and HfO₂ in the ground electronic states have C_{2v} symmetry. These are closed-shell systems; thus the symmetry is ¹A₁. The structures of anionic ZrO₂ and HfO₂ maintain the C_{2v} symmetry and the excess electron occupies a fully symmetric orbital (a₁); see Figure 2. Thus the symmetry of the open-shell electronic anionic states is ²A₁. The calculated bond lengths, OMO bond angles, adiabatic electron affinities, and harmonic vibration frequencies for ZrO₂ and HfO₂ are listed in Table 2. The reported values AEA include vibrational zero-point energy contributions. The CCSD(T)/L values of AEA are 1.62 and 2.05 eV for ZrO₂ and HfO₂, respectively, thus in excellent agreement with the corresponding measured values of 1.64 ± 0.03 and 2.14 ± 0.03 eV. There are only small differences in the values of AEA obtained with the S and L basis sets. Including spin-orbit coupling effects may further improve the agreement with

TABLE 2: Calculated M–O Bond Lengths (Å), OMO Bond Angles (deg), Adiabatic Electron Affinities (eV), and Vibrational Frequencies (cm⁻¹) for ZrO₂ and HfO₂^{*}

system	method	M–O	∠OMO	AEA	<i>v</i> ₁	<i>v</i> ₂	<i>v</i> ₃
ZrO ₂	CCSD(T)/L	1.797	109.6	1.62	887	281	835
	CCSD(T)/S	1.816	109.4	1.67	876	272	842
	B3LYP/SBKJ	1.806	108.0	1.85	906	295	854
ZrO ₂ ⁻	CCSD(T)/L	1.833	111.7	-	839	266	785
	CCSD(T)/S	1.853	111.9	-	829	255	790
	B3LYP/SBKJ	1.843	110.3	-	850	272	799
HfO ₂	CCSD(T)/L	1.815	109.9	2.05	869	266	801
	CCSD(T)/S	1.826	109.8	2.07	859	254	805
	B3LYP/SBKJ	1.797	107.3	2.32	898	293	821
HfO ₂ ⁻	CCSD(T)/L	1.855	114.3	-	819	242	752
	CCSD(T)/S	1.867	115.1	-	808	224	753
	B3LYP/SBKJ	1.833	111.6	-	844	255	772

^{*} The values of AEA include vibrational zero-point energy corrections. *v*₁ is the symmetric stretching mode, *v*₂ is the bending mode, and *v*₃ is the asymmetric stretching mode. “L” and “S” stand for the “large” and “small” basis sets, see text. For “SBKJ”, see ref 22.

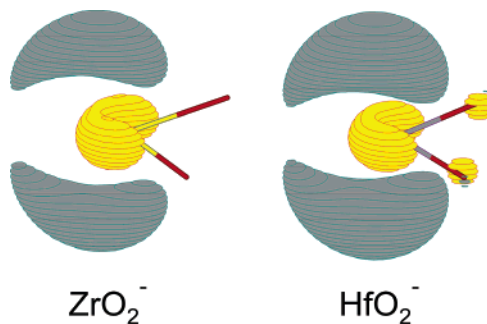


Figure 2. Excess electron in MO₂⁻ (M = Zr, Hf) occupying an a₁-symmetry orbital dominated by the M’s *ns* and (*n* – 1)*d* orbitals.

experiment for the Hf systems. The B3LYP values of AEA are overestimated with respect to the CCSD(T) results by 0.2–0.3 eV, which is typical for this exchange-correlation functional.^{32,33}

Our calculations confirm that the neutral ZrO₂ and HfO₂ have C_{2v} symmetry and a very similar bond length and ∠OMO.^{14,15} The M–O distances calculated at the CCSD(T)/L level are 1.797 Å for ZrO₂ and 1.815 Å for HfO₂, thus ca. 0.03–0.04 Å longer than the microwave spectroscopy predictions.^{14,15} The bond lengths are sensitive to the selection of one-electron basis set (L vs S) and the computational method (CCSD(T) vs B3LYP). The CCSD(T)/L values of ∠OMO of 109.6° and 109.9° are in excellent agreement with the previous findings of 108.11 ± 0.08° and 107.51 ± 0.01° for ZrO₂¹⁴ and HfO₂,¹⁵ respectively.

The calculated, harmonic, CCSD(T)/L frequencies for the symmetrical stretching mode of 887 cm⁻¹ (ZrO₂) and 869 cm⁻¹ (HfO₂) are consistent with the 887 ± 40 cm⁻¹ value resulting from the photoelectron spectra. However, the more accurate results from matrix infrared measurements¹³ of 884.3 cm⁻¹ (ZrO₂) and 883.4 cm⁻¹ (HfO₂) reveal that the calculated values might be inaccurate by ca. 15–20 cm⁻¹. The calculated harmonic CCSD(T)/L frequencies for the asymmetrical stretching mode are also inaccurate by ca. 20 cm⁻¹. The calculated frequency for the bending mode of ZrO₂ (281 cm⁻¹) agrees well with the 290 cm⁻¹ value determined from the inertial defect.¹⁴ The B3LYP vibrational force constants are systematically larger for ZrO₂ than for HfO₂ and so are the reduced masses resulting in very similar values of vibrational frequencies for the two molecules.

Upon the excess electron attachment the M–O bond lengths increase by ca. 0.04 Å and ∠OMO’s increase by 2–4°; see Table 2. The differences in geometries between the neutral and the anion are along the symmetrical stretching mode, *v*₁, and

the bending mode, ν_2 . The frequencies of all vibrational modes decrease upon the excess electron attachment with a larger shift (30–50 cm^{-1}) for the stretching modes and a smaller shift of 15–25 cm^{-1} for the bending mode.

ZrO₂ and HfO₂ are polar molecules with the experimentally measured dipole moments of 7.80¹⁴ and 7.92¹⁵ D, respectively. The calculated dipole moments are consistent with experiment in predicting a larger polarity of HfO₂ than of ZrO₂, but the absolute values of dipole moments are overestimated. Indeed, the corresponding B3LYP/S values are 8.00 and 8.06 D. The overestimation is even larger at the CCSD/S level with the corresponding values being 8.40 and 8.60 D. The effective charge on the metal, determined from the Mulliken population analysis with the B3LYP/SBKJ wave functions, is +1.15 and +1.10 e, for HfO₂ and ZrO₂, respectively. The excess electron is found to localize on the metal atom, where the positive pole of the dipole is (Figure 2). An excess electron bound by a polar molecule, which does not contain a transition metal atom, is typically described by a fully symmetric sp-type hybrid orbital; see ref 34 for numerous examples. In the case of ZrO₂ and HfO₂, however, the *ns* and (*n* – 1)*d* orbitals are available on the metal atom, whereas the *np* orbitals are higher in energy. The excess electron is then described by a fully symmetric sd-type hybrid orbital with *a*₁ symmetry (Figure 2).

The low lying electronic states of the neutral ZrO₂ and HfO₂ were characterized at the TDDFT/B3LYP/S level of theory. For both systems, the lowest excited singlet and triplet states are of B₁ symmetry, with the b₁ orbital localized on the metal atom. The more stable ³B₁ states are at 2.15 and 1.55 eV with respect to the ground singlet state for ZrO₂ and HfO₂, respectively. The related ¹B₁ states are less stable by 0.07–0.08 eV. Thus the excited electronic states of the neutral do not contribute to the photoelectron spectra recorded with the 3.493 eV photons.

Discussion

The significant electron affinity difference between ZrO₂ and HfO₂, combined with the lack of a measurable difference in their ν_1 vibrational frequencies and very similar molecular geometries, appears to indicate electronic structure rather than size or bonding effects as the primary basis for reactivity and stability differences between ZrO₂ and HfO₂. The difference in stability of the ZrO₂/Si and HfO₂/Si interfaces with respect to formation of metal silicides was interpreted in terms of a larger stability of (i) HfO₂ than ZrO₂ and (ii) zirconium rather than hafnium silicides.¹⁸ The current results shed new light on differences in electronic structure of ZrO₂ and HfO₂.

Recent computational results on various polymorphs of HfO₂ and ZrO₂ indicate that the former is more ionic than the latter.³⁵ The former also has a larger band gap across all polymorphs. These results are consistent with the finding that the calculated heat of formation for the monoclinic phase is larger by 0.60 eV/formula unit for HfO₂ than for ZrO₂, with the experimental difference being 0.49 eV.¹⁷ The difference in ionicity is also confirmed by dipole moments of HfO₂ and ZrO₂, 7.92 and 7.80 D, respectively.^{15,14} A difference in the dipole moment might contribute to the different values of AEA for HfO₂ and ZrO₂; see Tables 1 and 2 and Figure 1. All these findings are consistent with a small difference in the electronegativity of Zr and Hf: 1.4 and 1.3, respectively, according to Pauling's scale.³⁶

How important is the lanthanide contraction for Hf? It has recently been demonstrated for various polymorphs of MO₂ that the volume per formula unit is smaller for HfO₂ than for ZrO₂, as if the ionic radius was smaller for “Hf(+4)” than for “(Zr(+4))”.³⁵ The difference was 3.9% for the most stable monoclinic

phase. This result is surprising because usually for congeneric elements an increase in the atomic number leads to an increase of the atomic or ionic radius. For typical elements from the second and third transition metal rows such an increase is reduced by the electron occupation of the 4*f* and relativistic effects, whereas for Zr and Hf the relative sizes are apparently reversed, as in the case of monovalent coin metals.³⁷ Indeed, the recommended ionic radius for “Hf(+4)” is smaller by 0.01 Å than that for “Zr(+4)”,¹² which qualitatively confirms the structural predictions for bulk phases. For the molecular systems, however, the measured M–O distance is larger for ZrO₂ (1.7710 ± 0.0007 Å)¹⁴ than for HfO₂ (1.7764 ± 0.0004 Å).¹⁵ Clearly, the parallelism between structural properties of bulk phases and molecular systems is limited.

The neutral ZrO₂ and HfO₂ are highly polar and the excess electron is described by a sd-type hybrid orbital localized on the metal atom. In the case of HfO₂[–] small amplitudes can be also identified on oxygens (Figure 2). The availability of (*n* – 1)*d* orbitals makes the charge distribution of an excess electron different than in anions of polar molecules that do not contain a transition metal atom. One might only speculate what the charge distribution of an excess electron would be in polar molecules with available (*n* – 2)*f* orbitals, such as CeO₂ or BaO anions.

Because Ti, Zr, and Hf are all in the same group of the periodic table, it is also interesting to compare the electron affinities and vibrational frequencies of ZrO₂ and HfO₂ with those of TiO₂. Wu and Wang³⁸ reported the photoelectron spectrum of TiO₂[–]. They found the adiabatic electron affinity of TiO₂ to be 1.59 ± 0.03 eV and the frequency of ν_1 to be 940 ± 40 cm^{-1} . These properties of TiO₂, HfO₂, and ZrO₂ are compared in Table 1. Note that ZrO₂ and HfO₂ have essentially identical vibrational frequencies, whereas the ν_1 vibrational frequency of TiO₂ differs from them. This indicates differences in bonding strength and reduced masses between TiO₂ and ZrO₂ (HfO₂). Consistent with this, the atomic and ionic radii of zirconium and hafnium are the same to within 0.01 Å, whereas the ionic radius of Ti(+4) is smaller by 0.1 Å than those of Zr(+4) and Hf(+4).¹² The comparison reverses, however, when adiabatic electron affinities are compared. The electron affinities of TiO₂ and ZrO₂ are rather similar, differing by only 0.05 eV, whereas the electron affinities of HfO₂ and ZrO₂ differ substantially, i.e., by 0.50 eV. These comparisons reinforce the implication that differences in the electronic structures of Hf and Zr are at the root of chemical differences between ZrO₂ and HfO₂. This points to the nonnegligible role of *f*-electrons and relativistic effects in the chemistry of hafnium compounds.

It may be useful to mention that there are other examples among atomic metals, metal–ligand complexes, and metal dimer and cluster anions, in which the excess electron occupies a metal *s* orbital, which likewise shows an increased electron affinity for the third transition series congener, mirroring the trend observed here.³⁹ This pattern has been ascribed to relativistic effects, resulting in more strongly bound *s* electrons in the third transition series. Because the orbital occupied by the extra electron in ZrO₂[–] and HfO₂[–] has a significant metal *s* character (Figure 2), the reported values of AEA are consistent with this trend. This observation supports our conclusions that the presence of *f* electrons in the third transition series affects valence electronic structure controlled by the 5*d* and 6*s* orbitals.

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