Unveiling the coexistence of structural isomers in the hydrolysis of ZrO_2 : A combined computational and photoelectron spectroscopy study

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Abstract

High-resolution anion photoelectron spectroscopy of the ZrO_3H_2^- and ZrO_3D_2^- anions and complementary electronic structure calculations are used to investigate the reaction between zirconium dioxide and a single water molecule, $\text{ZrO}_2^{0/-} + \text{H}_2\text{O}$. Experimental spectra of ZrO_3H_2^- and ZrO_3D_2^- were obtained using slow photoelectron

velocity-map imaging (cryo-SEVI), revealing the presence of two dissociative adduct conformers and yielding insight into the vibronic structure of the corresponding neutral species. Franck-Condon simulations for both the *cis*- and *trans*-dihydroxide structures are required to fully reproduce the experimental spectrum. Additionally, it was found that water-splitting is stabilized more by ZrO_2 than TiO_2 , suggesting Zr-based catalysts are more reactive toward hydrolysis.

Introduction

Zirconium dioxide (ZrO_2) is an extensively studied material with widespread applications in medicine,¹⁻³ gas-cleaning technology,⁴ ceramics,⁵⁻⁷ corrosion-resistant materials,⁸⁻¹⁰ and heterogeneous catalysis.¹¹ As in the case of titania (TiO_2), photosensitization of water on a ZrO_2 electrode has inspired the development of ZrO_2 based technologies to exploit its photocatalytic properties for solar-powered hydrogen fuel cells.¹²⁻¹⁶ Despite significant effort, these technologies are not yet viable, in part due to the limited mechanistic knowledge needed for further development.¹⁷ Specifically, a more complete understanding of the interaction between ZrO_2 and water is required to develop these devices. Here, we present high-resolution photoelectron spectra of the ZrO_3H_2^- anion in tandem with electronic structure calculations, providing insight into the simplest reaction of $\text{ZrO}_2^{0/-}$ with water.

There is a vast body of work on the surface chemistry of metal oxides aimed at understanding water oxidation,¹⁸⁻²⁵ with a considerable number of studies probing the ZrO_2 surface specifically.²⁶⁻³⁰ From this body of work, it has become clear that defect sites play a critical role in the catalytic process,³¹⁻³⁶ thus investigating the interaction of water molecules at these sites is crucial for gaining insights into the water splitting mechanism. Such studies are challenging, however, owing to the difficulty of synthesizing and probing molecular-scale structures embedded with low density on bulk surfaces.³⁷⁻⁴⁵ Overcoming the hurdles of generating and controlling defect sites can be bypassed by preparing and studying gas-phase metal oxide clusters, as these species show structural motifs that mimic the geometries of

common defect sites.^{46–48} Further, the relatively small size of these systems makes them computationally tractable, enabling experimentalists and theorists to determine their electronic structure, geometries, and catalytic reaction mechanisms - a task not viable from bulk studies alone.^{49–53} There has been substantial progress made in understanding the structure and reactivity of small metal oxide clusters,^{54–59} including several studies on the interaction between titanium dioxide clusters and water molecules.^{60–63}

Of particular relevance is the work of Zheng and co-workers, who performed anion photoelectron spectroscopy (PES) on the anionic $(\text{TiO}_2)(\text{H}_2\text{O})_{0-7}$ clusters and inferred that dissociative adsorption of water occurs to form a hydroxide species.⁶¹ We recently reinvestigated the $(\text{TiO}_2^-)(\text{H}_2\text{O})$ system using slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI), a high-resolution form of anion PES, coupled with detailed computational simulations.⁶⁴ That work shows evidence that the dissociative adduct, *cis*-dihydroxide $\text{TiO}(\text{OH})_2^-$, is a planar C_{2v} structure that is energetically favored over a molecularly adsorbed complex and other lower-symmetry dissociative species.

Though still a Group IV metal oxide, ZrO_2 has been studied less extensively than titania.^{65–71} Within the bulk framework, Sayama et al.¹⁷ initiated significant interest in the field with the discovery of the photocatalytic decomposition of water on pure ZrO_2 powder following UV irradiation. Later, it was shown that adding a carbonate-based salt such as NaHCO_3 or Na_2CO_3 to an aqueous ZrO_2 suspension increased the gas evolution rate in the photocatalytic decomposition of water.⁷² The interaction of water with bulk zirconia surfaces has been characterized and investigated by X-ray powder diffraction, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, calorimetry, and Fourier-transform infrared spectroscopy (FTIR),^{73–76} along with periodic density functional theory (DFT) calculations.^{77–80} Notably, the FTIR investigation by Holmes and co-workers⁷⁶ of water sorption on ZrO_2 found bands corresponding to chemisorbed OH groups, suggesting that water bound to the surface of ZrO_2 forms a $\text{OZr}(\text{OH})_2$ -like structure.

Bare $(\text{ZrO}_2)_n^{0/-}$ clusters have been extensively studied using PES,^{81–83} matrix-IR spec-

troscopy,⁸⁴ Fourier-transform microwave spectroscopy,⁸⁵ laser-induced fluorescence,⁸⁶ resonant multi-photon ionization,⁸⁶ dispersed fluorescence,⁸⁶ and computational methods.^{81,84,87–90} Despite this growing body of work, there is no experimental data on the reactions of these clusters with a water molecule, though computational studies by Dixon et al.⁹¹ on the $(\text{ZrO}_2)_n + \text{H}_2\text{O}$ ($n=1-4$) reaction find these clusters are capable of splitting water. That work shows the dissociative adduct to be more stable than the molecularly adsorbed species by roughly 200 kJ/mol, at both the DFT and coupled cluster levels of theory, in agreement with experimental observations on bulk zirconia.⁸⁰ Further, the optimized geometries of the dissociative adduct were found to adopt only a *cis*-hydroxide geometry in contrast with computational results for the $\text{TiO}_2^{0/-} + \text{H}_2\text{O}$ dissociative adducts, where both *cis* and *trans* isomers were identified.^{64,92}

Here, we present a combined computational and experimental investigation of ZrO_3H_2^- and ZrO_3D_2^- , thereby probing fundamental aspects of the $\text{ZrO}_2^{0/-} + \text{H}_2\text{O}$ gas-phase reaction. The dense and highly resolved vibrational structure seen in the cryo-SEVI spectra is only reproduced if detachment from both low-lying isomers of the $\text{ZrO}(\text{OH})_2^{0/-}$ system, the *cis*-dihydroxide and *trans*-dihydroxide dissociative adducts, are considered. Additionally, the electron affinity of the neutral *cis*-dihydroxide structure and adiabatic electron affinity (ADE) of the anionic *trans*-dihydroxide are reported along with vibrational frequencies of both neutral structures. Further, agreement between experiment and theory facilitates not only the structural determination of these clusters, but also provides insight into the differences between the hydrolysis reactions of TiO_2 and ZrO_2 .

Methods

Experimental Methods

The cryo-SEVI method has been described in detail previously.^{93–95} In this work, ZrO_3H_2^- ions were formed using the same modified ablation ion source used to generate TiO_3H_2^- .⁶⁴ Clus-

ters are produced via a pulse from the frequency-doubled output of a 20 Hz Nd:YAG (2-3 mJ/pulse) that strikes a rotating and translating zirconium target, forming a plasma that is carried through an 80 mm long, 2 mm diameter channel by a pulse of helium gas (150 psi backing pressure, 60 μ s pulse width) from an Even-Lavie valve.⁹⁶ This expansion allows for the plasma to cool and condense to form charged and neutral molecules and clusters. These then pass through a 1 mm slit into a second channel, 90 mm long, and 2 mm in diameter. In this second channel, a pulsed Series 9 General Valve introduces helium bubbled through room temperature H₂O or D₂O (15 psi backing pressure, pulse width $\sim$ 160 μ s) allowing for the ablation products to cool further, react with H₂O or D₂O, and finally expand into vacuum.

The ions then pass through a radiofrequency (RF) hexapole ion guide and a RF quadrupole mass filter before being directed into a linear RF octupole ion trap held at 5 K and filled with a buffer gas mixture of 20:80 H₂:He. Collisions with the cold buffer gas result in effective vibrational, rotational, and electronic cooling of the ions, leading to internal temperatures of around 10 K.^{95,97} After $\sim$ 40 ms, the clusters are extracted into an orthogonal Wiley-McLaren time of flight mass spectrometer⁹⁸ and focused into the interaction region of a velocity-map imaging (VMI) electrostatic lens assembly,^{99,100} where they are photodetached by vertically polarized light from a pulsed laser.

The detachment laser configuration is based on the output of a dye laser pumped by the second harmonic of a Nd:YAG laser operating at 20 Hz. For photon energies above $\sim$ 1.3 eV (10,500 cm⁻¹, 950 nm), the output of the dye laser is used without modification. For energies below 1.3 eV, the output of the dye laser is focused into a 63-cm long Raman cell containing described previously,⁶⁴ resulting in tunable photon energies ranging from $\sim$ 1.0 to 1.3 eV (8,000-10,500 cm⁻¹).

The resulting photoelectrons are projected onto a 2D detector comprising two chevron-stacked microchannel plates coupled to a phosphor screen, which is photographed by a CCD camera after each laser shot.¹⁰¹ Each image is analyzed for individual electron events for

which the centroids are calculated and binned in a 2200×2200 grid.¹⁰² Slight deviations from circularity in the accumulated images are corrected using the circulization algorithm described by Gascooke et al.¹⁰³ The three-dimensional electron velocity distribution is then reconstructed from the circularized images using the Maximum Entropy Velocity Legendre Reconstruction (MEVELER) algorithm.¹⁰⁴ The radial position of features in the reconstructed image is related to electron kinetic energy (eKE) by acquiring VMI images for detachment from atomic Ni^- and O^- at several photon energies.^{105,106}

The VMI spectrometer has an approximately constant resolving power, $\Delta\text{eKE}/\text{eKE}$,⁹⁹ yielding the best eKE resolution for slow electrons. As such, a SEVI spectrum is acquired by first taking an overview spectrum at a relatively high photon energy before tuning the detachment laser to energies slightly above features of interest. This procedure results in a collection of high-resolution spectra over narrow energy windows that are concatenated and scaled to match intensities in the overview spectrum, which is less sensitive to variation of the photodetachment cross section with photon energy. Spectra are plotted as a function of electron binding energy (eBE), given by $\text{eBE} = h\nu - \text{eKE}$.

In addition to the eKE distributions, VMI allows for the determination of photoelectron angular distributions (PADs) associated with each detachment transition, given by¹⁰⁷

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{tot}}{4\pi} [1 + \beta P_2(\cos \theta)] \quad (1)$$

where σ_{tot} is the total detachment cross section, $P_2(x)$ is the second-order Legendre polynomial, θ is the angle of the outgoing photoelectron velocity vector with respect to the laser polarization axis, and β is the anisotropy parameter. The anisotropy parameter, which ranges from -1 (perpendicular detachment) to +2 (parallel detachment), reflects the angular momentum of the detached electron and is thus tied to the electronic character of each photodetachment transition.¹⁰⁸

Computational Methods

A variety of DFT-based model chemistries were used to identify possible minimum energy structures along the anionic and neutral $\text{ZrO}_2 + \text{H}_2\text{O}$ surface. Initial benchmark work was carried out by comparing six different functionals (B3LYP, B3PW91, M06, M06L, PBE1PBE and ω B97XD) and two basis sets (def2tzvp and the Stuttgart/Cologne ECP28MHF (SC)) resulting in 12 different model chemistries.^{109–120} Tables S1-S6 summarize the results obtained from these benchmark calculations. Preliminary results suggested meaningful differences in normal mode frequencies and vertical excitation energies. After a detailed inspection of these results and comparison with the experimental data presented here, we determined that the ω B97XD/SC model chemistry best reproduces the observed relative experimental energies and vibrational frequencies.

A number of electronic states for the anion and neutral species were investigated. For the anion, doublet and quartet spin states were considered, while singlet and triplet states were included for the neutral. All model chemistries predicted lowest spin states (neutral singlet and anion doublet) to be energetically most stable. Excited-state calculations were carried out using the same model chemistry within the (linear response) time-dependent DFT (TDDFT) formalism.^{121–123}

All calculations were carried out using a local development version of the GAUSSIAN suite of electronic structure programs.¹²⁴ Stability was tested on all converged Kohn–Sham determinants.^{125,126} Standard methods were used for optimizing molecular geometries,¹²⁷ and the nature of located stationary points were verified using analytical second-derivative calculations.^{128,129} Franck–Condon (FC) spectra were generated using the implementation by Bloino, Barone, and co-workers.^{130,131} Simulated PES spectra, including FC progressions, were adjusted to align with the experimental spectra after shifting DFT force constants of the neutral state. Full details, including scaling factors and shifting parameters, are provided in the SI. Characterization of electron detachment was facilitated by the Natural Ionization Orbital (NIO) model.¹³² The NIO model provides the Dyson orbital for a Δ SCF

treatment of electron detachment and, within the sudden approximation, provides insight to electron relaxation accompanying electron detachment. The NIO model has been successfully employed in a number of recent studies involving similar systems.^{64,132,133}

Results and Discussion

Experiment

Figure 1: Cryo-SEVI spectra of ZrO_3H_2 . The overview spectrum (blue, $h\nu = 10,747 \text{ cm}^{-1}$) is vertically offset from the high-resolution traces (black, variable photon energies).

Figure 2: Cryo-SEVI spectra of ZrO_3D_2 . The overview spectrum (blue, $h\nu = 9,802 \text{ cm}^{-1}$) is vertically offset from the high-resolution traces (black, variable photon energies).

Cryo-SEVI spectra of ZrO_3H_2^- and ZrO_3D_2^- are shown in Figs. 1 and 2, respectively. In both figures, overview spectra, taken with relatively high photon energies, are displayed in blue atop composite high-resolution scans in black taken with various photon energies. While the overview spectrum displays structure for eBEs up to $\sim 10,750 \text{ cm}^{-1}$, high resolution scans were collected only out to $\sim 10,000 \text{ cm}^{-1}$; see Fig. S1 in the SI for the full overview spectrum. These high-resolution traces highlight structure covering eBEs from $9,300$ to $10,000 \text{ cm}^{-1}$, revealing a number of transitions (A-V and A-T in ZrO_3H_2 and ZrO_3D_2 , respectively) that correspond to detachment to different vibrational levels of the neutral ZrO_3H_2 and ZrO_3D_2 species. Peaks as narrow as 4 cm^{-1} fwhm are reported, owing to strong photoelectron signal at low eKEs where resolution is highest. It should be noted that ions with $m/z = 140$ were chosen despite the possible contribution from $^{92}\text{ZrO}_3$ as well as the target $^{90}\text{ZrO}_3\text{H}_2^-$ species; the electron affinity of ZrO_3 has not been experimentally determined, but is calculated to be 3.06 eV , substantially higher than the photon energies employed in this work ($< 1.35 \text{ eV}$), and thus should not contribute to the reported spectra.

The sharp onset of structure at peak A, the vibrational origin, allows for determination of the EAs for ZrO_3H_2 and ZrO_3D_2 as 1.1636(5) and 1.1616(7) eV, respectively. Beyond peak A, we observe a prominent doublet of peaks (B/C) residing just above 9,400 cm^{-1} in both spectra, split by $\sim 5 \text{ cm}^{-1}$. A similar doublet is observed near 9,800 cm^{-1} in both spectra (peaks O/P in the spectrum of ZrO_3H_2 and S/T in ZrO_3D_2). Owing to the doublet structure, assignment by inspection is not straightforward, as discussed below.

Experimentally determined parameters are reported in Tables 1 and 2 for ZrO_3H_2 and ZrO_3D_2 , respectively, while peak positions, widths, and assignments are listed in Tables S13 and S14. Measured PADs of peaks A, B, C, and D are shown in Fig. S10 of the SI. All PADs reported display a similar trend - features have an anisotropy parameter, β , near zero at low eKE that becomes increasingly positive as the eKE rises.

Calculations

The structures found in our previous work⁶⁴ on the $\text{TiO}_2^{0/-} + \text{H}_2\text{O}$ reaction were used as starting points for minimum energy structure searches. Figure 3 shows the minimum energy structures found on the anionic and neutral ZrO_3H_2 potential energy surfaces, along with corresponding zero-point corrected energies relative to **1-1a**. Cartesian coordinates for these optimized structures are provided in the SI. In agreement with previously reported work by Dixon and co-workers⁹¹ and similar to our previous report on $\text{TiO}(\text{OH})_2$,⁶⁴ a dissociative adduct (**1-1a'**) with a *cis*-OH geometry was found to be the lowest energy neutral structure. Similarly, the **1-1a** geometry was found to be the lowest energy anion structure. Two other structures were identified for both neutral and anion states, labeled **1-1b** (*trans*-OH) and **1-1c** (molecularly adsorbed). Structure **1-1b** differs from **1-1a** by rotation of one hydroxide ligand and lies only 0.07 eV above the global minimum. Thus the two structures, **1-1a** and **1-1b**, are conformers related by OH bond rotation with a barrier in the anion of 0.016 eV. The neutral *trans*-hydroxide **1-1b'** lies at 0.07 eV above neutral **1-1a'**, while the lowest energy neutral molecularly adsorbed species is 3.11 eV above the anion minimum while its anion is

2.14 eV above the minimum of the anionic *cis* structure. Interestingly, unlike $\text{TiO}_3\text{H}_2^{0/-}$, the $\text{ZrO}_3\text{H}_2^{0/-}$ dissociative adducts are found to have non-planar optimized structures.

Figure 3: Optimized geometries of anionic and neutral ZrO_3H_2 found with $\omega\text{B97XD/SC}$. Energies are provided relative to the **1-1a** geometry of the anion and include zero-point corrections. Geometric parameters are also provided.

Given its high relative energy with respect to the dissociative adducts, the molecularly adsorbed adduct **1-1c** was excluded from further consideration. The calculated adiabatic detachment energies (ADEs) for **1-1a** and **1-1b**, 1.04 eV and 1.11 eV respectively, are both in good agreement with the experimental value of 1.1636(5) eV, determined by the position of peak A. NIO analysis for both **1-1a** and **1-1b** shows the detached electron originates in the anion HOMO, which is localized on Zr and strongly resembles a metal d_{z^2} orbital (Fig. 4). The similarity of the NIO results suggests that both structures should have similar photodetachment cross-sections and angular distributions.

Figure 4: NIO describing the electron detachment from the anion of **1-1a** (a) and **1-1b** (b) to corresponding ground electronic state of the neutral species.

Analysis

Assignment of spectra

Figure 5: Cryo-SEVI spectra of ZrO_3H_2^- overlaid with Franck-Condon stick spectra for the **1-1a** (red) and **1-1b** (blue) isomers.

Figure 6: Cryo-SEVI spectra of ZrO_3D_2^- overlaid with Franck-Condon stick spectra for the **1-1a** (red) and **1-1b** (blue) isomers.

To examine the possible contributions of the two candidate structures and whether one or both of them are responsible for the observed experimental detachment transitions, we considered FC simulations for electron detachment from both isomers, shown as red sticks for **1-1a** and blue sticks for **1-1b** in Fig. 5 and 6, using experimental frequencies when available. Simulated spectra using unscaled frequencies are shown in Figs. S2-5 in the SI. Each isomer has distinct FC progressions; that corresponding to **1-1a** shows a short progression in the out-of-plane bending mode, ν_{12} ($\omega_{12a} = 73 \text{ cm}^{-1}$), while that of **1-1b** shows an extended progression for the same mode ($\omega_{12b} = 67 \text{ cm}^{-1}$), owing to a greater change in the dihedral angle between **1-1b** and **1-1b'** than in the **1-1a** manifold as outlined in Tables S7 and S8. Further, FC-simulations for the **1-1b** manifold show considerably more structure due to activity along the ν_{10} and ν_{11} O-H wagging modes ($\omega_{10b} = 167 \text{ cm}^{-1}$, $\omega_{11b} = 115 \text{ cm}^{-1}$) that serve as the isomerization coordinate to the **1-1a'** structure.

As shown in Fig. 5, simulation of detachment from **1-1a** only replicates features A, B, P, Q, and V of the cryo-SEVI spectrum of ZrO_3H_2 , failing to capture the majority of

the observed structure. Conversely, simulations for the **1-1b** isomer capture the majority of the spectral structure, but fail to replicate the doublets B/C and O/P observed in the high-resolution traces. A composite of both simulations replicates the observed experimental spectrum well, including the doublet structure of peaks B/C and O/P, suggesting the presence of both isomers in the experiment.

In addition to enabling identification of the anion isomers, the well-resolved vibrational structure in the spectra allows us to determine vibrational frequencies of the neutral **1-1a'** and **1-1b'** isomers of $\text{ZrO}(\text{OH})_2$ and $\text{ZrO}(\text{OD})_2$, as reported in Tables 1 and 2, respectively. Remarkably, we are able to distinguish features arising from transitions along the ν_{12} modes of the **1-1a'** and **1-1b'** isomers, despite their frequencies differing by only 6 cm^{-1} . One dominant pattern in the spectrum (peaks C, E, and H in both $\text{ZrO}(\text{OH})_2$ and $\text{ZrO}(\text{OD})_2$) corresponds to a progression of the ν_{12} out-of-plane bend of the **1-1b'** isomer with a vibrational frequency of $73(3) \text{ cm}^{-1}$ ($69(3) \text{ cm}^{-1}$ in $\text{ZrO}(\text{OD})_2$). Further, agreement between experimental and computational results allows for assignment of peaks D, F, and N to the vibrational fundamentals of the ν_{11} , ν_{10} , and ν_8 modes of the **1-1b'** isomer, allowing for the determination of their vibrational frequencies as $115(3)$, $167(2)$, and $358(3) \text{ cm}^{-1}$ ($110(4)$, $155(3)$, and $347(5) \text{ cm}^{-1}$ in $\text{ZrO}(\text{OD})_2$).

Table 1: Summary of electronic and vibrational energies for neutral $\text{ZrO}(\text{OH})_2$ extracted from the cryo-SEVI experiment compared to the (unscaled) results from $\omega\text{B97XD/SC}$ calculations.

	1-1a'		1-1b'	
	Exp	Theor	Exp	Theor
ADE (eV)	1.1636(5)	1.04	1.1636(5)	1.04
$\nu_5 \text{ (cm}^{-1}\text{)}$	597(2)	622.8		
$\nu_6 \text{ (cm}^{-1}\text{)}$	429(6)	513.7		
$\nu_8 \text{ (cm}^{-1}\text{)}$			358(3)	416.8
$\nu_9 \text{ (cm}^{-1}\text{)}$	388(4)	428.8		
$\nu_{10} \text{ (cm}^{-1}\text{)}$			167(2)	191.0
$\nu_{11} \text{ (cm}^{-1}\text{)}$	167(2)	170.3	115(3)	141.0
$\nu_{12} \text{ (cm}^{-1}\text{)}$	67(3)	87.6	73(3)	75.0

Table 2: Summary of electronic and vibrational energies for neutral ZrO(OD)_2 extracted from the cryo-SEVI experiment compared to the (unscaled) results from $\omega\text{B97XD/SC}$ calculations.

	1-1a'		1-1b'	
	Exp	Theor	Exp	Theor
ADE (eV)	1.1616(7)	1.04	1.1616(7)	1.04
ν_6 (cm^{-1})	425(3)	395.2		
ν_8 (cm^{-1})			347(5)	316.4
ν_9 (cm^{-1})	384(5)	323.8		
ν_{10} (cm^{-1})			155(3)	181.1
ν_{11} (cm^{-1})	155(3)	159.9	110(4)	117.3
ν_{12} (cm^{-1})	65(3)	82.4	69(3)	70.9

A similar treatment can be applied for the detachment transition to **1-1a'**. Features B, F, P, Q, and V correspond to transitions involving one quanta along the ν_{12} , ν_{11} , ν_9 , ν_6 , and ν_5 normal coordinates, allowing for determination of their vibrational frequencies as 67(3), 167(2), 388(4), 429(6), and 597(2) cm^{-1} in ZrO(OH)_2 . The same vibrational modes are observed in the deuterated spectra, with the exception of the ν_5 mode owing to the truncation of this spectra before its appearance, appearing as features B, F, P, and T with vibrational frequencies of 65(3), 155(3), 384(5), and 425(3) cm^{-1} . The remaining structure in both spectra corresponds to transitions with excitation along multiple vibrational modes; details of these assignments can be found in Tables S13 and S14 of the SI for ZrO(OH)_2 and ZrO(OD)_2 , respectively.

Given that the **1-1b** simulations reproduce most of the spectral features observed, one needs to consider if it is possible to interpret the spectrum with this isomer alone. Previous cryo-SEVI studies have uncovered myriad non-Born Oppenheimer behavior in small molecules that fail to be reproduced by FC simulations, most notably vibronic coupling.^{134–137} The signatures of this phenomenon in cryo-SEVI are well established, arising due to borrowed electronic character from an excited state.^{64,135,137–141} Among these signatures are differing photoelectron angular distributions between transitions that are allowed only through vibronic coupling and those that are FC-allowed.

In the present work, doublet splittings of peaks B and P are notably absent from the **1-1b** simulations. For peak B to correspond to a vibronic coupling induced transition, as opposed to a Franck-Condon allowed transition within the **1-1a** band of transitions as listed in Table 1, would require a non-totally-symmetric vibrational frequency on the order of 70 cm^{-1} in the **1-1b'** isomer. No calculated frequency is within a factor of 2 of this value; indeed, the best candidate is the ν_{11} mode ($\omega_{11} = 141\text{ cm}^{-1}$) corresponding with the transition that produces peak D. Further, the PADs of features B/C do not differ from one another, as shown in Fig. S10. The similar PADs for detachment from both isomers is in agreement with our NIO analyses that suggest the detached electron resides in a similar orbital for **1-1a** and **1-1b**, resulting in outgoing electrons with similar partial wave composition. As the measured PADs reflect the angular momentum of the detached electron, they are tied to the electronic character of each photodetachment transition and are thus expected not to differ between detachment from **1-1a** or **1-1b**.

An alternative option is that peaks B and P could report on transitions from or to excited anionic or neutral states. The calculated values of the lowest anion and neutral excited electronic states, 1.5 and 4.5 eV above their respective ground states, render them inaccessible as the cryogenic nature of the cryo-SEVI experiment produces ions with electronic temperatures on the order of 10K (0.86 meV)^{134,142,143} and the photon energies employed in this experiment are $< 1.35\text{ eV}$.

As much of the structure in the **1-1b** FC simulation originates from the ν_{12} umbrella-mode, an alternative possibility for the origin of the doublet structure of peaks B/C and O/P is inversion doubling. Such a process occurs when a vibrational mode distorts a molecule such that it breaks planar symmetry, leading to a double-well potential surface splitting the vibrational levels supported by such a surface, most famously occurring in the umbrella mode of ammonia.¹⁴⁴ If such a double-well surface is capable of supporting both a left and right wavefunction on the anionic potential and both sides of the well are populated, this will give rise to a doublet of transitions following photodetachment.^{145,146} Our calculations

indicate that the inversion barrier for the **1-1b** isomer is 1.64 eV, owing to the large dihedral angle of this structure. Considering the high barrier, we expect for contributions from tunneling splitting to be too small to observe. The structure observed in the cryo-SEVI spectra presented is thus most reasonably assigned to photodetachment from two different anion isomers, each resulting in a neutral isomer of similar molecular symmetry and overall structure.

The observation of multiple structural isomers in a cryo-SEVI experiment has been observed previously in the cryo-SEVI spectra of Ti_2O_4^- and Zr_2O_4^- .¹⁴⁷ In that work, the spectra were assigned to detachment from anionic structural isomers with relative energetics (6.7 kJ/mol and 10.5 kJ/mol, respectively) that are comparable to those reported in the present study (7.5 kJ/mol).¹⁴⁷ The assignment to two different isomers of Ti_2O_4^- and Zr_2O_4^- was suggested and supported by FC progressions with dichotomous PADs and notably different onsets resulting from unique adiabatic detachment energies for each isomer. As the structures observed here are conformers related by a bond rotation, it is unsurprising that neither the PADs or ADEs differ substantially in the present work, suggesting the **1-1a** and **1-1b** isomers have ADEs lying within our experimental resolution (2 cm^{-1}). This result is consistent with the calculated energetics that show the energy difference between the *cis* and *trans* conformers are virtually identical in the anion and neutral.

Comparison to $\text{TiO}(\text{OH})_2$

The presence of two low-lying anion isomers of the $\text{ZrO}_2 + \text{H}_2\text{O}$ dissociative adduct is in contrast with our previous findings for the Ti-containing analogue of this system, in which we observe detachment solely from the **1-1a** isomer.⁶⁴ In that work, the cryo-SEVI spectrum is relatively sparse, displaying less structure in the first $2,000\text{ cm}^{-1}$ than is observed in the 800 cm^{-1} of spectral structure presented here and shows no signs of contribution from the **1-1b** isomer. Given that the experimental conditions to generate both species differ only by the identity of the metal target used to generate clusters of interest, the observation of two

isomers in the present study is particularly interesting.

Our calculations show that the energetics of both Ti- and Zr- containing **1-1a** and **1-1b** anions are nearly identical with the **1-1a** structure more stable than **1-1b** by 0.08 and 0.07 eV in the Ti- and Zr- systems, respectively. Further, the calculated barriers to interconversion between the *cis*-**1-1a** and *trans*-**1-1b** structures are similar for these two systems. Here, we calculate the *cis*-to-*trans* barrier for $\text{TiO}(\text{OH})_2^-$ to be 803 cm^{-1} (0.100 eV) while the *trans*-to-*cis* barrier is 159 cm^{-1} (0.020 eV). For $\text{ZrO}(\text{OH})_2^-$, these barriers are calculated as 737 cm^{-1} (0.091 eV) and 130 cm^{-1} (0.016 eV), respectively, suggesting one might expect similar populations of conformers in each experiment.

Given the similarity in the geometries, energetics, and barriers of these clusters, it is likely that the observation of both the **1-1a** and **1-1b** species in $\text{ZrO}(\text{OH})_2^-$ but not $\text{TiO}(\text{OH})_2^-$ results from disparate ion temperatures in these two systems. Such a disparity could result from the method by which these clusters are generated – laser ablation of a metal target generates a hot plasma that condenses to form the clusters of interest. It is well established that the cluster condensation process results in significant heating,¹⁴⁸ as the binding energy of each additional atom is deposited into the cluster. Given that such growth events can occur late in the clustering channel and the bond enthalpy of Zr-O exceeds that of Ti-O by nearly 100 kJ/mol,¹⁴⁹ it is likely these two systems will have differing thermal populations prior to entering the cryogenic trap, with $\text{ZrO}(\text{OH})_2^-$ hotter than $\text{TiO}(\text{OH})_2^-$. The increased temperature will enhance the population of higher lying isomers relative to the global minimum structure and such a distribution is likely to be mirrored in the trap, as buffer gas cooling is known to favor kinetic trapping.^{150,151} Such a result would agree with previous cryo-SEVI studies of clusters, where we find trapping of ions in low-lying local minima.^{147,152,153}

It should also be noted that in the case of TiO_3H_2 , the appearance of the umbrella mode (ν_{12} here, ν_8 in TiO_3H_2) was ascribed to vibronic coupling,⁶⁴ while no such non-Born-Oppenheimer process is observed here, despite similar energetics for the states involved. In that work, the Ti-containing analogue was determined to be a planar C_{2v} structure in both

its neutral and anionic forms, resulting in a FC-forbidden umbrella mode, as the out-of-plane motion of this vibrational mode breaks the C_{2v} symmetry of the molecule. Conversely, the Zr-containing systems presently observed are non-planar C_s structures with dihedral angles ranging from 20° - 30° whose molecular symmetry is not perturbed by the umbrella mode. While this motion can only be observed through vibronic coupling in the Ti-system, such a mode is readily accessible for ZrO_3H_2 without violating the Born-Oppenheimer approximation.

Reactivity of MO_2 with H_2O

The cryo-SEVI spectrum of unreacted ZrO_2^- has been previously reported, giving an electron affinity of 1.6397(5) eV for the singlet ground state of ZrO_2 .¹⁵⁴ The electron affinity of the $ZrO(OH)_2$ dissociative adducts reported here are lower by nearly 0.5 eV, suggesting the neutral $ZrO_2 + H_2O \rightarrow ZrO(OH)_2$ reaction is more exothermic than its anionic counterpart. The reaction with water to form the dissociative $ZrO(OH)_2$ adduct stabilizes neutral ZrO_2 more than it does the anion, implying that the neutral, which has a zirconium center with a +4 oxidation state, is more reactive toward water than anionic ZrO_2 where Zr has an oxidation state of +3. A similar trend in electron affinities was seen for TiO_2 and $TiO(OH)_2$. Taken together, these results suggest that this charge effect likely derives from donation of electron density from the incoming water molecule to the metal center, favoring a higher oxidation state.⁶⁴

Notably, the measured difference in EA for the Ti-containing system was roughly 0.3 eV, suggesting that the addition of water to the Zr-based system stabilizes ZrO_2 relative to its anion a full 0.2 eV (19.2 kJ/mol) more than the Ti-based system. In turn, this implies an increased reactivity of the ZrO_2 moiety compared to TiO_2 . As single site catalyst studies have found high photocatalytic activity attributed to the increased reactivity of single TiO_2 structures anchored onto porous surfaces,^{155,156} the results presented here show promise for the development of Zr-based analogues with increased efficiency. While it is difficult to make

a direct comparison between the chemistry occurring at the bulk surface and the gas-phase $\text{ZrO}_2^{0/-}$ reaction, the trends reported here do reflect the electrochemical behavior of the bulk,¹⁵⁶ especially with respect to a higher oxidation state resulting in a more energetically favorable interaction with water.

Conclusion

A joint DFT and high-resolution photoelectron study has been used to investigate the hydrolysis of $\text{ZrO}_2^{0/-}$. Experimental spectra of ZrO_3H_2^- are reported using slow electron velocity map imaging of cryogenically cooled anions, revealing the presence of two dissociative adduct conformers and yielding insights into the vibronic structure and energetics of the corresponding neutral species. The high resolution afforded by this technique reveals a dense vibrational manifold dissimilar to the well-separated peaks obtained in the cryo-SEVI study of the titanium analogue.⁶⁴ Franck-Condon simulations for both the *cis*- (**1-1a**) and *trans*-dihydroxide (**1-1b**) structures are required to fully reproduce the complicated cryo-SEVI spectra, representing the first report of the *trans*-hydroxide (**1-1b**) structure of the ZrO_3H_2 system. The appearance of these two isomers is attributed to differing cluster temperatures prior to reaction with H_2O or D_2O , resulting in an enhancement of the population of structure **1-1b** in ZrO_3H_2^- . Further, the greater stabilization of water-splitting by ZrO_2 than TiO_2 suggests higher reactivity for Zr-based catalysts, offering new insights into the development of single-site catalysts for H_2 production.

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