Unveiling the coexistence of *cis-* and *trans*isomers in the hydrolysis of ZrO₂: A coupled DFT and high-resolution photoelectron spectroscopy study

Cite as: J. Chem. Phys. **153**, 244308 (2020); https://doi.org/10.1063/5.0037636 Submitted: 15 November 2020 . Accepted: 02 December 2020 . Published Online: 30 December 2020

🔟 Ali Abou Taka, ២ Mark C. Babin, Xianghai Sheng, ២ Jessalyn A. DeVine, ២ Daniel M. Neumark, and ២ Hrant P. Hratchian







J. Chem. Phys. **153**, 244308 (2020); https://doi.org/10.1063/5.0037636 © 2020 Author(s). **153**, 244308

View Onlin

Export Citation

Unveiling the coexistence of *cis*and *trans*-isomers in the hydrolysis of ZrO₂: A coupled DFT and high-resolution photoelectron spectroscopy study

Cite as: J. Chem. Phys. 153, 244308 (2020); doi: 10.1063/5.0037636
Submitted: 15 November 2020 • Accepted: 2 December 2020 •
Published Online: 30 December 2020

Ali Abou Taka,¹ D Mark C. Babin,² Xianghai Sheng,¹ Jessalyn A. DeVine,^{2,a)} Daniel M. Neumark,^{2,3,b)} And Hrant P. Hratchian^{1,c)}

AFFILIATIONS

¹ Department of Chemistry & Chemical Biology, Center for Chemical Computation and Theory, University of California, Merced, California 95343, USA

²Department of Chemistry, University of California, Berkeley, California 94720, USA

³Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

^{a)}**Current address**: Department of Dynamics at Surfaces, Max-Planck Institute for Biophysical Chemistry, Am Faßberg 11, 37077 Göttingen, Germany. ^{b)}dneumark@berkeley.edu

^{c)}Author to whom correspondence should be addressed: hhratchian@ucmerced.edu

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, $ZrO_2^{0/-} + H_2O$. Experimental spectra of $ZrO_3H_2^-$ and $ZrO_3D_2^-$ were obtained using slow photoelectron velocity-map imaging of cryogenically cooled anions, 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 TiO₂, suggesting Zr-based catalysts are more reactive toward hydrolysis.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0037636

I. INTRODUCTION

Zirconium dioxide (ZrO₂) 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 (TiO₂), photosensitization of water on a ZrO₂ electrode has inspired the development of ZrO₂ based technologies to exploit its photocatalytic properties for solar-powered hydrogen fuel cells.^{12–16} Despite significant efforts, 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 ZrO₂ 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 specifically probing the ZrO₂ surface.^{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} Furthermore, 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 (TiO₂) (H₂O)₀₋₇ clusters and inferred that dissociative adsorption of water occurs to form a hydroxide species.⁶¹ We recently reinvestigated the (TiO₂⁻) (H₂O) 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 TiO(OH)₂⁻, is a planar C_{2ν} structure that is energetically favored over a molecularly adsorbed complex and other lower-symmetry dissociative species.

Though still a group IV metal oxide, ZrO₂ has been studied less extensively than titania.65-71 Within the bulk framework, Sayama and Arakawa¹⁷ initiated significant interest in the field with the discovery of the photocatalytic decomposition of water on pure ZrO₂ powder following UV irradiation. Later, it was shown that adding a carbonate-based salt such as NaHCO3 or Na2CO3 to an aqueous ZrO₂ 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 (FTIR) spectroscopy,⁷³⁻⁷⁶ along with periodic density functional theory (DFT) calculations.77-80 Notably, the FTIR investigation by Agron and co-workers⁷⁶ of water sorption on ZrO₂ found bands corresponding to chemisorbed OH groups, suggesting that water bound to the surface of ZrO₂ forms a OZr(OH)₂-like structure.

Bare $(ZrO_2)_n^{0/-}$ clusters have been extensively studied using PES,^{81–83} matrix-IR spectroscopy,⁸⁴ Fourier-transform microwave spectroscopy,⁸⁵ laser-induced fluorescence,⁸⁶ resonant multi-photon ionization,⁸⁶ dispersed fluorescence,⁸⁶ and computational meth-ods.^{81,84,87–90} Despite this growing body of work, there are no experimental data on the reactions of these clusters with a water molecule, though computational studies by Fang *et al.*⁹¹ on the $(ZrO_2)_n + H_2O$ (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 Furthermore, the optimized geometries of the dissociative adduct were found to adopt only a cishydroxide geometry in contrast with computational results for the $TiO_2^{0/-} + H_2O$ 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 the fundamental aspects of the $ZrO_2^{0/-}$ + H₂O 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 $ZrO(OH)_2^{0/-}$ system, the *cis*-dihydroxide and *trans*dihydroxide dissociative adducts, is 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. Furthermore, 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 TiO₂ and ZrO₂.

A. 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 TiO₃H₂^{-.64} Clusters are produced via a pulse from the frequency-doubled output of a 20 Hz Nd:YAG (2 mJ/pulse-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 µs 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 ~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 ~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 ~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 described previously,⁶⁴ resulting in tunable photon energies ranging from ~1.0 eV to 1.3 eV (8000 cm⁻¹-10 500 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 circularization 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, $\Delta eKE/eKE$,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 eBE = $h\nu - eKE$.

In addition to the eKE distributions, VMI allows for the determination of photoelectron angular distributions (PADs) associated with each detachment transition, given by 107

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

where σ_{tot} is the total detachment cross section, $P_2(x)$ is the secondorder 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

B. Computational methods

A variety of DFT-based model chemistries were used to identify possible minimum energy structures along the anionic and neutral $ZrO_2 + H_2O$ 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

The 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 was 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 supplementary material. Characterization of electron detachment was facilitated by the Natural Ionization Orbital (NIO) model.¹³² The NIO model provides the Dyson orbital for a \triangle SCF treatment of electron detachment and, within the sudden approximation, provides insight into electron relaxation accompanying electron detachment. The NIO model has been successfully employed in a number of recent studies involving similar systems.^{64,132,7}

II. RESULTS AND DISCUSSION

A. Experiment

Cryo-SEVI spectra of $ZrO_3H_2^-$ and $ZrO_3D_2^-$ are shown in Figs. 1 and 2, respectively. In Figs. 1 and 2, 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 the structure for eBEs up to ~10750 cm⁻¹, high resolution scans were collected only out to ~10000 cm⁻¹ (see Fig. S1 in the supplementary material for the full overview spectrum). These high-resolution traces highlight structure covering eBEs from 9300 cm⁻¹ to 10000 cm⁻¹, revealing a number of transitions (A-V and A-T in ZrO₃H₂ and ZrO₃D₂, respectively) that correspond to detachment to different vibrational levels of the neutral ZrO₃H₂ and ZrO₃D₂ species. Peaks as narrow as 4 cm⁻¹ fwhm are reported, owing to the 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 ⁹²ZrO₃⁻ as well as the target ⁹⁰ZrO₃H₂⁻ species; the electron affinity of



FIG. 1. Cryo-SEVI spectra of ZrO_3H_2 . The overview spectrum (blue, $h\nu$ = 10747 cm⁻¹) is vertically offset from the high-resolution traces (black, variable photon energies).



FIG. 2. Cryo-SEVI spectra of ZrO_3D_2 . The overview spectrum (blue, $h\nu = 9802 \text{ cm}^{-1}$) is vertically offset from the high-resolution traces (black, variable photon energies).

 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 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 9400 cm⁻¹ in both spectra, split by ~5 cm⁻¹. A similar doublet is observed near 9800 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 I and II 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 supplementary material. All PADs reported display a similar

TABLE I. Summary of electronic and vibrational energies for neutral $ZrO(OH)_2$ extracted from the cryo-SEVI experiment compared to the (unscaled) results from ω B97XD/SC calculations.

	1-1a'		1–1b′	
	Expt.	Theory	Expt.	Theory
ADE (eV)	1.1636(5)	1.04	1.1636(5)	1.04
$v_5 ({\rm cm}^{-1})$	597(2)	622.8		
$v_6 ({\rm cm}^{-1})$	429(6)	513.7		
$v_8 ({\rm cm}^{-1})$			358(3)	416.8
$v_9 ({\rm cm}^{-1})$	388(4)	428.8		
$v_{10} ({\rm cm}^{-1})$			167(2)	191.0
$v_{11} (\text{cm}^{-1})$	167(2)	170.3	115(3)	141.0
$v_{12} ({\rm cm}^{-1})$	67(3)	87.6	73(3)	75.0

TABLE II. Summary of electronic and vibrational energies for neutral $2rO(OD)_2$
extracted from the cryo-SEVI experiment compared to the (unscaled) results from
ω B97XD/SC calculations.

	1-1a'		1–1b'	
	Expt.	Theory	Expt.	Theory
ADE (eV)	1.1616(7)	1.04	1.1616(7)	1.04
$v_6 ({\rm cm}^{-1})$	425(3)	395.2		
$v_8 ({\rm cm}^{-1})$			347(5)	316.4
$v_9 (cm^{-1})$	384(5)	323.8		
$v_{10} ({\rm cm}^{-1})$			155(3)	181.1
$v_{11} (cm^{-1})$	155(3)	159.9	110(4)	117.3
$v_{12} ({\rm cm}^{-1})$	65(3)	82.4	69(3)	70.9

trend—features have an anisotropy parameter, β , near zero at low eKE that becomes increasingly positive as the eKE rises.

B. Calculations

The structures found in our previous work⁶⁴ on the $TiO_2^{0/-}$ + H₂O reaction were used as starting points for minimum energy structure searches. Figure 3 shows the minimum energy structures found on the anionic and neutral ZrO₃H₂ potential energy surfaces, along with corresponding zero-point corrected energies relative to 1-1a. Cartesian coordinates for these optimized structures are provided in the supplementary material. In agreement with previously reported work by Dixon and co-workers⁹¹ and similar to our previous report on $TiO(OH)_2$,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, and its anion is 2.14 eV above the minimum of the anionic *cis* structure. Interestingly, unlike $TiO_3H_2^{0/-}$, the $ZrO_3H_2^{0/-}$ dissociative adducts are found to have non-planar optimized structures.

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.



FIG. 3. Optimized geometries of anionic and neutral ZrO_3H_2 found with ω B97XD/SC. Energies are provided relative to the **1–1a** geometry of the anion and include zero-point corrections. Geometric parameters are also provided.

III. ANALYSIS

A. Assignment of spectra

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 Figs. 5 and 6, using experimental frequencies when available. Simulated spectra using unscaled frequencies are shown in Figs. S2–S5 of the supplementary material. Each isomer has distinct FC progressions; the one corresponding to **1–1a** shows a short progression in the out-of-plane bending mode, v_{12} ($\omega_{12a} = 73$ cm⁻¹), while that of **1–1b** shows an extended progression for the same mode ($\omega_{12b} = 67$ 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. Furthermore, FC-simulations for the **1–1b** manifold show considerably

more structure due to activity along the v_{10} and v_{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 the 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'



FIG. 4. NIO describing the electron detachment from the anion of 1–1a (a) and 1–1b (b) to the corresponding ground electronic state of the neutral species.



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



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

isomers of ZrO(OH)₂ and ZrO(OD)₂, as reported in Tables I and II, respectively. Remarkably, we are able to distinguish features arising from transitions along the v_{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 ZrO(OH)₂ and ZrO(OD)₂] corresponds to a progression of the v_{12} out-of-plane bend of the **1–1b'** isomer with a vibrational frequency of 73(3) cm⁻¹ [69(3) cm⁻¹ in ZrO(OD)₂]. Furthermore, agreement between experimental and computational results allows for assignment of peaks D, F, and N to the vibrational fundamentals of the v_{11} , v_{10} , and v_8 modes of the **1–1b'** isomer, allowing for the determination of their vibrational frequencies as 115(3), 167(2), and 358(3) cm⁻¹ [110(4), 155(3), and 347(5) cm⁻¹ in ZrO(OD)₂].

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 quantum along the v_{12} , v_{11} , v_9 , v_6 , and v_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 v_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 supplementary material 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 I, 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 v_{11} mode ($\omega_{11} = 141$ cm⁻¹) corresponding to the transition that produces peak D. Furthermore, 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 are 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 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 eV 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 10 K (0.86 meV), 95,97,134 and the photon energies employed in this experiment are <1.35 eV.

As much of the structure in the 1-1b FC simulation originates from the v_{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.¹⁴ If such a double-well surface is capable of supporting both the left and right wavefunctions on the anionic potential and both sides of the well are populated, this will give rise to a doublet of transitions following photodetachment.^{143,144} 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 Ti₂O₄⁻ and Zr₂O₄^{-.82} 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).⁸² The assignment to two different isomers of Ti₂O₄⁻ and Zr₂O₄⁻ 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 is virtually identical in the anion and neutral.

B. Comparison to TiO(OH)₂

The presence of two low-lying anion isomers of the ZrO_2 + H_2O dissociative adduct is in contrast with our previous findings for the Ti-containing analog 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 2000 cm⁻¹ than that is observed in the 800 cm⁻¹ of the 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 Zrcontaining **1–1a** and **1–1b** anions are nearly identical with the **1–1a** structure more stable than **1–1b** by 0.08 eV and 0.07 eV in the Tiand Zr-systems, respectively. Furthermore, 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 $TiO(OH)_2^-$ to be 803 cm⁻¹ (0.100 eV), while the *trans*to-*cis* barrier is 159 cm⁻¹ (0.020 eV). For $ZrO(OH)_2^-$, 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 $ZrO(OH)_2^-$ but not $TiO(OH)_2^-$ 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,¹⁴⁵ 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,¹⁴⁶ it is likely these two systems will have differing thermal populations prior to entering the cryogenic trap, with $ZrO(OH)_2^-$ hotter than $TiO(OH)_2^-$. 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.^{147,148} Such a result would agree with previous cryo-SEVI studies of clusters, where we find trapping of ions in low-lying local minima.⁸

It should also be noted that in the case of TiO₃H₂, the appearance of the umbrella mode (v_{12} here and v_8 in TiO₃H₂) 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 analog was determined to be a planar C₂, structure in both its neutral and anionic forms, resulting in an FC-forbidden umbrella mode, as the out-of-plane motion of this vibrational mode breaks the C₂, symmetry of the molecule. Conversely, the Zr-containing systems presently observed are non-planar C_s structures with dihedral angles ranging from 20° to 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 ZrO₃H₂ without violating the Born–Oppenheimer approximation.

C. Reactivity of MO₂ with H₂O

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 .⁸³ The electron affinity of the $ZrO(OH)_2$ dissociative adducts reported here is 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 TiO₂ 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 TiO₂. As single site catalyst studies have found high photocatalytic activity attributed to the increased reactivity of single TiO₂ structures anchored onto porous surfaces,^{151,152} the results presented here show promise for the development of Zr-based analogs with increased efficiency. While it is difficult to make a direct comparison between the chemistry occurring at the bulk surface and the gas-phase $ZrO_2^{0/-}$ reaction, the trends reported here do reflect the electrochemical behavior of the bulk,¹⁵² especially with respect to a higher oxidation state, resulting in a more energetically favorable interaction with water.

IV. CONCLUSION

A joint DFT and high-resolution photoelectron study has been used to investigate the hydrolysis of $ZrO_2^{0/-}$. Experimental spectra of ZrO₃H₂⁻ 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 analog.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 ZrO₃H₂ system. The appearance of these two isomers is attributed to differing cluster temperatures prior to reaction with H₂O or D₂O, resulting in an enhancement of the population of structure 1-1b in $ZrO_3H_2^-$. Furthermore, the greater stabilization of water-splitting by ZrO₂ than TiO₂ suggests higher reactivity for Zr-based catalysts, offering new insights into the development of single-site catalysts for H₂ production.

SUPPLEMENTARY MATERIAL

See the supplementary material for details regarding electronic structure and Franck–Condon calculations summarized in Tables S1–S16 and Figs. S1–S10.

AUTHORS' CONTRIBUTIONS

A.A.T. and M.C.B. contributed equally to this work.

ACKNOWLEDGMENTS

A.A.T., X.S., and H.P.H. are grateful for support from the National Science Foundation under Grant No. CHE-1848580 and computer time on the MERCED high-performance computing cluster, which was supported by the National Science Foundation under Grant No. ACI-1429783. D.M.N. thanks the Air Force Office of Scientific Research for funding this research under Grant No. FA9550-19-1-0051. M.C.B. thanks the Army Research Office for a National Defense Science and Engineering Graduate fellowship.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

¹N. A. Patil and B. Kandasubramanian, "Biological and mechanical enhancement of zirconium dioxide for medical applications," Ceram. Int. **46**, 4041 (2019).

²L. Hingsammer, M. Grillenberger, M. Schagerl, M. Malek, and S. Hunger, "Biomechanical testing of zirconium dioxide osteosynthesis system for Le Fort I advancement osteotomy fixation," J. Mech. Behav. Biomed. Mater. 77, 34 (2018). ³T.-W. Chen, A. Sivasamy Vasantha, S.-M. Chen, D. A. Al Farraj, M. Soliman Elshikh, R. M. Alkufeidy, and M. M. Al Khulaifi, "Sonochemical synthesis and fabrication of honeycomb like zirconium dioxide with chitosan modified electrode for sensitive electrochemical determination of anti-tuberculosis (TB) drug," Ultrason. Sonochem. **59**, 104718 (2019).

⁴P. Sjoholm, D. B. Ingham, M. Lehtimaki, L. Perttu-Roiha, H. Goodfellow, and H. Torvela, "Gas-cleaning technology," in *Industrial Ventilation Design Guidebook* (Elsevier, 2001), pp. 1197–1316.

⁵S. Dudczig, D. Veres, C. G. Aneziris, E. Skiera, and R. W. Steinbrech, "Nano- and micrometre additions of SiO₂, ZrO₂ and TiO₂ in fine grained alumina refractory ceramics for improved thermal shock performance," Ceram. Int. 38, 2011 (2012).
⁶C. G. Aneziris, S. Dudczig, N. Gerlach, H. Berek, and D. Veres, "Thermal shock performance of fine grained Al₂O₃ ceramics with TiO₂ and ZrO₂ additions for refractory applications," Adv. Eng. Mater. 12, 478 (2010).

⁷M. Chen, C. Lu, and J. Yu, "Improvement in performance of MgO-CaO refractories by addition of nano-sized ZrO₂," J. Eur. Ceram. Soc. **27**, 4633 (2007).

⁸V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides* (Cambridge University Press, 1996).

⁹I. Shishkovsky, I. Yadroitsev, P. Bertrand, and I. Smurov, "Alumina-zirconium ceramics synthesis by selective laser sintering/melting," Appl. Surf. Sci. **254**, 966 (2007).

¹⁰L. L. Fehrenbacher, "Stabilized zirconium dioxide and hafnium dioxide compositions," US patent 3,634,113 (January 11, 1972).

¹¹G. A. Gogotsi, "Deformational behaviour of ceramics," J. Eur. Ceram. Soc. 7, 87 (1991).

¹²H.-G. Lintz and C. G. Vayenas, "Solid ion conductors in heterogeneous catalysis," Angew. Chem., Int. Ed. Engl. 28, 708 (1989).

¹³E. F. Sverdrup, A. D. Glasser, and D. H. Archer, "Fuel cell comprising a stabilized zirconium oxide electrolyte and a doped indium or tin oxide cathode," US patent 3,558,360 (January 26, 1971).

¹⁴A. J. Nozik, "Photoelectrolysis of water by solar radiation," US patent 4,011,149 (March 8, 1977).

¹⁵A. B. Stambouli and E. Traversa, "Solid oxide fuel cells (SOFCS): A review of an environmentally clean and efficient source of energy," Renewable Sustainable Energy Rev. 6, 433 (2002). ¹⁶A. Iannaci, T. Pepè Sciarria, B. Mecheri, F. Adani, S. Licoccia, and A. D'Epifanio, "Power generation using a low-cost sulfated zirconium oxide based cathode in single chamber microbial fuel cells," J. Alloys Compd. **693**, 170 (2017).

¹⁷K. Sayama and H. Arakawa, "Photocatalytic decomposition of water and photocatalytic reduction of carbon dioxide over zirconia catalyst," J. Phys. Chem. 97, 531 (1993).

¹⁸L. Yang, H. Zhou, T. Fan, and D. Zhang, Semiconductor Photocatalysts for Water Oxidation: Current Status and Challenges (Royal Society of Chemistry, 2014), Vol. 16, pp. 6810–6826.

¹⁹M. Muhler, R. Schlögl, and G. Ertl, "The nature of the iron oxide-based catalyst for dehydrogenation of ethylbenzene to styrene 2. Surface chemistry of the active phase," J. Catal. **138**, 413 (1992).

²⁰N. Perry and T. Ishihara, "Roles of bulk and surface chemistry in the oxygen exchange kinetics and related properties of mixed conducting perovskite oxide electrodes," <u>Materials 9</u>, 858 (2016).

²¹ F. Seker, K. Meeker, T. F. Kuech, and A. B. Ellis, "Surface chemistry of prototypical bulk II-VI and III-V semiconductors and implications for chemical sensing," Chem. Rev. **100**, 2505 (2000).

²²H. Darmstadt, L. Sümmchen, J.-M. Ting, U. Roland, S. Kaliaguine, and C. Roy, "Effects of surface treatment on the bulk chemistry and structure of vapor grown carbon fibers," Carbon 35, 1581 (1997).

²³H. A. Al-Abadleh, "Review of the bulk and surface chemistry of iron in atmospherically relevant systems containing humic-like substances," RSC Adv. 5, 45785 (2015).

 $^{\mathbf{24}}$ J. Marcos, R. Buitrago, and E. Lombardo, "Surface chemistry and catalytic activity of La_{1-y}M_yCoO₃ perovskite (M = Sr or Th): 1. Bulk and surface reduction studies," J. Catal. **105**, 95 (1987).

²⁵W. Prellier, M. P. Singh, and P. Murugavel, "The single-phase multiferroic oxides: From bulk to thin film," J. Phys.: Condens. Matter 17, R803 (2005).

²⁶Z. Xu and J. R. Kitchin, "Relationships between the surface electronic and chemical properties of doped 4D and 5D late transition metal dioxides," J. Chem. Phys. **142**, 104703 (2015).

²⁷J. Horkans and M. W. Shafer, "An investigation of the electrochemistry of a series of metal dioxides with rutile-type structure: MoO₂, WO₂, ReO₂, RuO₂, OsO₂, and IrO₂," J. Electrochem. Soc. **124**, 1202 (1977).

²⁸Y. Tang, S. Zhao, B. Long, J.-C. Liu, and J. Li, "On the nature of support effects of metal dioxides MO₂ (M = Ti, Zr, Hf, Ce, Th) in single-atom gold catalysts: Importance of quantum primogenic effect," J. Phys. Chem. C 120, 17514 (2016).
 ²⁹H. H. Kung, *Transition Metal Oxides: Surface Chemistry and Catalysis* (Elsevier, 1989), Vol. 45.

³⁰G. Busca and V. Lorenzelli, "Infrared spectroscopic identification of species arising from reactive adsorption of carbon oxides on metal oxide surfaces," Mater. Chem. 7, 89 (1982).

³¹ H. H. Kristoffersen, J. Ø. Hansen, U. Martinez, Y. Wei, J. Matthiesen, R. Streber, R. Bechstein, E. Lægsgaard, F. Besenbacher, B. Hammer *et al.*, "Role of steps in the dissociative adsorption of water on rutile TiO₂ (110)," Phys. Rev. Lett. **110**, 146101 (2013).

³²V. E. Henrich and P. A. Cox, "Fundamentals of gas-surface interactions on metal oxides," Appl. Surf. Sci. 72, 277 (1993).

³³M. Calatayud, A. Markovits, M. Menetrey, B. Mguig, and C. Minot, "Adsorption on perfect and reduced surfaces of metal oxides," Catal. Today 85, 125 (2003).

³⁴M. Daturi, C. Binet, S. Bernal, J. A. Pérez Omil, and J. Claude Lavalley, "FTIR study of defects produced in ZrO₂ samples by thermal treatment residual species into cavities and surface defects," J. Chem. Soc., Faraday Trans. **94**, 1143 (1998).

³⁵G. K. Chuah and S. Jaenicke, "The preparation of high surface area zirconia— Influence of precipitating agent and digestion," Appl. Catal., A 163, 261 (1997).

³⁶X. Xia, R. Oldman, and R. Catlow, "Computational modeling study of bulk and surface of yttria-stabilized cubic zirconia," Chem. Mater. **21**, 3576 (2009).

³⁷G. Haas, A. Menck, H. Brune, J. V. Barth, J. A. Venables, and K. Kern, "Nucleation and growth of supported clusters at defect sites: Pd/MgO (001)," Phys. Rev. B **61**, 11105 (2000).

³⁸K. R. Heim, S. T. Coyle, G. G. Hembree, J. A. Venables, and M. R. Scheinfein, "Growth of nanometer-size metallic particles on CaF₂ (111)," J. Appl. Phys. **80**, 1161 (1996).

J. Chem. Phys. **153**, 244308 (2020); doi: 10.1063/5.0037636 Published under license by AIP Publishing ³⁹J. A. Venables, "Nucleation growth and pattern formation in heteroepitaxy," Physica A **239**, 35 (1997).

⁴⁰G. Fahsold, A. Pucci, and K.-H. Rieder, "Growth of Fe on MgO (001) studied by He-atom scattering," Phys. Rev. B 61, 8475 (2000).

⁴¹E. I. Solomon, P. M. Jones, and J. A. May, "Electronic structures of active sites on metal oxide surfaces: Definition of the copper-zinc oxide methanol synthesis catalyst by photoelectron spectroscopy," Chem. Rev. **93**, 2623 (1993).

⁴²H. Yamamoto, N. Watanabe, A. Wada, K. Domen, and C. Hirose, "Adsorption and decomposition of formic acid on MgO (001) surface as investigated by temperature programmed desorption and sum-frequency generation spectroscopy: Recurrence induced defect sites," J. Chem. Phys. **106**, 4734 (1997).

⁴³Z. Wu, M. Li, J. Howe, H. M. Meyer III, and S. H. Overbury, "Probing defect sites on CeO₂ nanocrystals with well-defined surface planes by Raman spectroscopy and O₂ adsorption," Langmuir 26, 16595 (2010).

⁴⁴ M. J. Borda, A. R. Elsetinow, D. R. Strongin, and M. A. Schoonen, "A mechanism for the production of hydroxyl radical at surface defect sites on pyrite," Geochim. Cosmochim. Acta **67**, 935 (2003).

 45 J. Joubert, A. Salameh, V. Krakoviack, F. Delbecq, P. Sautet, C. Copéret, and J. M. Basset, "Heterolytic splitting of H₂ and Ch₄ on *y*-alumina as a structural probe for defect sites," J. Phys. Chem. B **110**, 23944 (2006).

⁴⁶H.-J. Zhai and L.-S. Wang, "Probing the electronic structure of early transition metal oxide clusters: Molecular models towards mechanistic insights into oxide surfaces and catalysis," Chem. Phys. Lett. **500**, 185 (2010).

⁴⁷A. Castleman, "Cluster structure and reactions: Gaining insights into catalytic processes," Catal. Lett. **141**, 1243 (2011).

⁴⁸S. M. Lang and T. M. Bernhardt, "Gas phase metal cluster model systems for heterogeneous catalysis," Phys. Chem. Chem. Phys. **14**, 9255 (2012).

⁴⁹R. O. Ramabhadran, J. E. Mann, S. E. Waller, D. W. Rothgeb, C. C. Jarrold, and K. Raghavachari, "New insights on photocatalytic H₂ liberation from water using transition-metal oxides: Lessons from cluster models of molybdenum and tungsten oxides," J. Am. Chem. Soc. **135**, 17039 (2013).

⁵⁰ R. Fagiani, X. Song, S. Debnath, S. Gewinner, W. Schöllkopf, K. R. Asmis, F. A. Bischoff, F. Müller, and J. Sauer, "Dissociative water adsorption by Al₃O₄⁺ in the gas phase," J. Phys. Chem. Lett. **8**, 1272 (2017).

⁵¹ K. Raghavachari and M. D. Halls, "Quantum chemical studies of semiconductor surface chemistry using cluster models," Mol. Phys. **102**, 381 (2004).

⁵²J. E. Mann, N. J. Mayhall, and C. C. Jarrold, "Properties of metal oxide clusters in non-traditional oxidation states," Chem. Phys. Lett. **525-526**, 1 (2012).

⁵³J. L. Mason, H. Harb, J. E. Topolski, H. P. Hratchian, and C. C. Jarrold, "Exceptionally complex electronic structures of lanthanide oxides and small molecules," Acc. Chem. Res. 52, 3265 (2019).

⁵⁴G. Zhang, H. Hattori, and K. Tanabe, "Aldol addition of acetone, catalyzed by solid base catalysts: Magnesium oxide, calcium oxide, strontium oxide, barium oxide, lanthanum (III) oxide and zirconium oxide," Appl. Catal. **36**, 189 (1988).

⁵⁵S. S. Atsu, M. A. Kilicarslan, H. C. Kucukesmen, and P. S. Aka, "Effect of zirconium-oxide ceramic surface treatments on the bond strength to adhesive resin," J. Prosthet. Dent. **95**, 430 (2006).

⁵⁶Y. Nakano, T. Iizuka, H. Hattori, and K. Tanabe, "Surface properties of zirconium oxide and its catalytic activity for isomerization of 1-butene," J. Catal. 57, 1 (1979).

⁵⁷D. M. Hausmann and R. G. Gordon, "Surface morphology and crystallinity control in the atomic layer deposition (ALD) of hafnium and zirconium oxide thin films," J. Cryst. Growth **249**, 251 (2003).

⁵⁸B. Bachiller-Baeza, I. Rodriguez-Ramos, and A. Guerrero-Ruiz, "Interaction of carbon dioxide with the surface of zirconia polymorphs," Langmuir 14, 3556 (1998).

⁵⁹A. Hess and E. Kemnitz, "Surface acidity and catalytic behavior of modified zirconium and titanium dioxides," Appl. Catal., A **149**, 373 (1997).

 60 T.-H. Wang, Z. Fang, N. W. Gist, S. Li, D. A. Dixon, and J. L. Gole, "Computational study of the hydrolysis reactions of the ground and first excited triplet states of small TiO₂ nanoclusters," J. Phys. Chem. C **115**, 9344 (2011).

⁶¹R.-Z. Li, H.-G. Xu, G.-J. Cao, X.-L. Xu, and W.-J. Zheng, "Interaction of TiO₂ with water: Photoelectron spectroscopy and density functional calculations," J. Chem. Phys. **139**, 184303 (2013).

⁶²H.-G. Xu, X.-N. Li, X.-Y. Kong, S.-G. He, and W.-J. Zheng, "Interaction of TiO⁺ with water: Infrared photodissociation spectroscopy and density functional calculations," Phys. Chem. Chem. Phys. **15**, 17126 (2013).

⁶³ M. L. Weichman, S. Debnath, J. T. Kelly, S. Gewinner, W. Schöllkopf, D. M. Neumark, and K. R. Asmis, "Dissociative water adsorption on gas-phase titanium dioxide cluster anions probed with infrared photodissociation spectroscopy," Top. Catal. 61, 92 (2018).

 64 J. A. DeVine, A. Abou Taka, M. C. Babin, M. L. Weichman, H. P. Hratchian, and D. M. Neumark, "High-resolution photoelectron spectroscopy of TiO₃H₂⁻: Probing the TiO₂⁻+H₂O dissociative adduct," J. Chem. Phys. **148**, 222810 (2018).

⁶⁵M. E. Geusic, M. D. Morse, S. C. O'Brien, and R. E. Smalley, "Surface reactions of metal clusters I: The fast flow cluster reactor," Rev. Sci. Instrum. 56, 2123 (1985).

⁶⁶X.-N. Wu, J.-B. Ma, B. Xu, Y.-X. Zhao, X.-L. Ding, and S.-G. He, "Collisioninduced dissociation and density functional theory studies of Co adsorption over zirconium oxide cluster ions: Oxidative and nonoxidative adsorption," J. Phys. Chem. A **115**, 5238 (2011).

⁶⁷Y.-X. Zhao, X.-L. Ding, Y.-P. Ma, Z.-C. Wang, and S.-G. He, "Transition metal oxide clusters with character of oxygen-centered radical: A DFT study," Theor. Chem. Acc. **127**, 449 (2010).

⁶⁸ J.-b. Ma, X.-n. Wu, Y.-x. Zhao, X.-l. Ding, and S.-g. He, "Experimental and theoretical study of hydrogen atom abstraction from C_2H_6 and C_4H_{10} by zirconium oxide clusters anions," Chin. J. Chem. Phys. **23**, 133 (2013).

⁶⁹J.-B. Ma, B. Xu, J.-H. Meng, X.-N. Wu, X.-L. Ding, X.-N. Li, and S.-G. He, "Reactivity of atomic oxygen radical anions bound to titania and zirconia nanoparticles in the gas phase: Low-temperature oxidation of carbon monoxide," J. Am. Chem. Soc. **135**, 2991 (2013).

⁷⁰X.-n. Wu, Y.-x. Zhao, S.-g. He, and X.-l. Ding, "Experimental and theoretical study of hydrogen atom abstraction from ethylene by stoichiometric zirconium oxide clusters," Chin. J. Chem. Phys. 22, 635 (2013).

 71 J. Kreutzer, P. Blaha, and U. Schubert, "Assessment of different basis sets and DFT functionals for the calculation of structural parameters, vibrational modes and ligand binding energies of $\rm Zr_4O_2$ (carboxylate)_{12} clusters," Comput. Theor. Chem. **1084**, 162 (2016).

 72 K. Sayama and H. Arakawa, "Effect of carbonate addition on the photocatalytic decomposition of liquid water over a ZrO₂ catalyst," J. Photochem. Photobiol., A **94**, 67 (1996).

⁷³ J. Li, J. Chen, W. Song, J. Liu, and W. Shen, "Influence of zirconia crystal phase on the catalytic performance of Au/ZrO₂ catalysts for low-temperature water gas shift reaction," Appl. Catal., A 334, 321 (2008).

⁷⁴S. Zinatloo-Ajabshir and M. Salavati-Niasari, "Facile route to synthesize zirconium dioxide (ZrO₂) nanostructures: Structural, optical and photocatalytic studies," J. Mol. Liq. **216**, 545 (2016).

⁷⁵H. F. Moafi, A. F. Shojaie, and M. A. Zanjanchi, "The comparison of photocatalytic activity of synthesized TiO₂ and ZrO₂ nanosize onto wool fibers," Appl. Surf. Sci. **256**, 4310 (2010).

⁷⁶P. A. Agron, E. L. Fuller, Jr., and H. F. Holmes, "Ir studies of water sorption on ZrO₂ polymorphs. I," J. Colloid Interface Sci. **52**, 553 (1975).

⁷⁷W. Piskorz, J. Gryboś, F. Zasada, P. Zapała, S. Cristol, J.-F. Paul, and Z. Sojka, "Periodic DFT study of the tetragonal ZrO₂ nanocrystals: Equilibrium morphology modeling and atomistic surface hydration thermodynamics," J. Phys. Chem. C **116**, 19307 (2012).

⁷⁸ M. Subhoni, K. Kholmurodov, A. Doroshkevich, E. Asgerov, T. Yamamoto, A. Lyubchyk, V. Almasan, and A. Madadzada, "Density functional theory calculations of the water interactions with ZrO₂ nanoparticles Y₂O₃ doped," J. Phys.: Conf. Ser. **994**, 012013 (2018).

⁷⁹C. M. Lousada, A. J. Johansson, T. Brinck, and M. Jonsson, "Reactivity of metal oxide clusters with hydrogen peroxide and water—A DFT study evaluating the performance of different exchange–correlation functionals," Phys. Chem. Chem. Phys. 15, 5539 (2013).

⁸⁰S. V. Ushakov and A. Navrotsky, "Direct measurements of water adsorption enthalpy on hafnia and zirconia," Appl. Phys. Lett. 87, 164103 (2005).

⁸¹W. Zheng, K. H. Bowen, J. Li, I. Dąbkowska, and M. Gutowski, "Electronic structure differences in ZrO₂ vs HfO₂," J. Phys. Chem. A **109**, 11521 (2005).

 82 J. B. Kim, M. L. Weichman, and D. M. Neumark, "Structural isomers of Ti₂O₄ and Zr₂O₄ anions identified by slow photoelectron velocity-map imaging spectroscopy," J. Am. Chem. Soc. **136**, 7159 (2014).

ARTICLE

⁸³ J. B. Kim, M. L. Weichman, and D. M. Neumark, "High-resolution anion photoelectron spectra of TiO_2^- , ZrO_2^- , and HfO_2^- obtained by slow electron velocity-map imaging," Phys. Chem. Chem. Phys. **15**, 20973 (2013).

⁸⁴G. V. Chertihin and L. Andrews, "Reactions of laser ablated titanium, zirconium, and hafnium atoms with oxygen molecules in condensing argon," J. Phys. Chem. **99**, 6356 (1995).

⁸⁵D. J. Brugh, R. D. Suenram, and W. J. Stevens, "Fourier transform microwave spectroscopy of jet-cooled ZrO₂ produced by laser vaporization," J. Chem. Phys. **111**, 3526 (1999).

⁸⁶A. Le, T. C. Steimle, V. Gupta, C. A. Rice, J. P. Maier, S. H. Lin, and C.-K. Lin, "The visible spectrum of zirconium dioxide, ZrO₂," J. Chem. Phys. **135**, 104303 (2011).

 87 S. Li and D. A. Dixon, "Molecular structures and energetics of the $(ZrO_2)_n$ and $(HfO_2)_n$ (n = 1-4) clusters and their anions," J. Phys. Chem. A **114**, 2665 (2010).

⁸⁸S. M. Woodley, S. Hamad, J. A. Mejías, and C. R. A. Catlow, "Properties of small TiO₂, ZrO₂ and HfO₂ nanoparticles," J. Mater. Chem. 16, 1927 (2006).

 89 M. Kaupp, "On the relation between π bonding, electronegativity, and bond angles in high-valent transition metal complexes," Chem. Eur. J. 5, 3631 (1999).

⁹⁰D. K. W. Mok, F.-t. Chau, J. M. Dyke, and E. P. F. Lee, "A combined *ab initio* and Franck–Condon simulation study of the photodetachment spectrum of ZrO₂⁻," Chem. Phys. Lett. **458**, 11 (2008).

 91 Z. Fang, M. D. Outlaw, K. K. Smith, N. W. Gist, S. Li, D. A. Dixon, and J. L. Gole, "Computational study of the hydrolysis reactions of small Mo₂ (M = Zr and Hf) nanoclusters with water," J. Phys. Chem. C **116**, 8475 (2012).

 92 M. Chen, T. P. Straatsma, and D. A. Dixon, "Molecular and dissociative adsorption of water on $(TiO_2)_n$ clusters, n = 1-4," J. Phys. Chem. A **119**, 11406 (2015).

⁹³ A. Osterwalder, M. J. Nee, J. Zhou, and D. M. Neumark, "High resolution photodetachment spectroscopy of negative ions via slow photoelectron imaging," J. Chem. Phys. **121**, 6317 (2004).

⁹⁴D. M. Neumark, "Slow electron velocity-map imaging of negative ions: Applications to spectroscopy and dynamics," J. Phys. Chem. A **112**, 13287 (2008).

⁹⁵C. Hock, J. B. Kim, M. L. Weichman, T. I. Yacovitch, and D. M. Neumark, "Slow photoelectron velocity-map imaging spectroscopy of cold negative ions," J. Chem. Phys. 137, 244201 (2012).

⁹⁶U. Even, J. Jortner, D. Noy, and N. Lavie, "Cooling of large molecules below 1 k and he clusters formation," J. Chem. Phys. **112**, 8068 (2000).

 97 J. B. Kim, C. Hock, T. I. Yacovitch, and D. M. Neumark, "Slow photoelectron velocity-map imaging spectroscopy of cold thiozonide (S3⁻)," J. Phys. Chem. A 117, 8126 (2013).

⁹⁸W. C. Wiley and I. H. McLaren, "Time-of-flight mass spectrometer with improved resolution," Rev. Sci. Instrum. 26, 1150 (1955).

⁹⁹A. T. J. B. Eppink and D. H. Parker, "Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen," Rev. Sci. Instrum. **68**, 3477 (1997).

¹⁰⁰M. L. Weichman, J. A. DeVine, D. S. Levine, J. B. Kim, and D. M. Neumark, "Isomer-specific vibronic structure of the 9-, 1-, and 2-anthracenyl radicals via slow photoelectron velocity-map imaging," Proc. Natl. Acad. Sci. U. S. A. 113, 1698 (2016).

¹⁰¹D. W. Chandler and P. L. Houston, "Two-dimensional imaging of stateselected photodissociation products detected by multiphoton ionization," J. Chem. Phys. 87, 1445 (1987).

¹⁰²M. B. Doyle, C. Abeyasera, and A. G. Suits, NuACQ, http://faculty.missouri. edu/suitsa/NuAqc.html.

¹⁰³J. R. Gascooke, S. T. Gibson, and W. D. Lawrance, "A 'circularisation' method to repair deformations and determine the centre of velocity map images," J. Chem. Phys. **147**, 013924 (2017).

¹⁰⁴B. Dick, "Inverting ion images without abel inversion: Maximum entropy reconstruction of velocity maps," Phys. Chem. Chem. Phys. **16**, 570 (2014).

 105 M. Scheer, C. A. Brodie, R. C. Bilodeau, and H. K. Haugen, Laser spectroscopic measurements of binding energies and fine-structure splittings of Co⁻, Ni⁻, Rh⁻, and Pd⁻," Phys. Rev. A **58**, 2051 (1998).

¹⁰⁶C. Blondel, W. Chaibi, C. Delsart, C. Drag, F. Goldfarb, and S. Kröger, "The electron affinities of O, Si, and S revisited with the photodetachment microscope," Eur. Phys. J. D 33, 335 (2005).

¹⁰⁷J. Cooper and R. N. Zare, "Angular distribution of photoelectrons," J. Chem. Phys. 48, 942 (1968).

¹⁰⁸A. Sanov, "Laboratory-frame photoelectron angular distributions in anion photodetachment: Insight into electronic structure and intermolecular interactions," Annu. Rev. Phys. Chem. **65**, 341 (2014).

¹⁰⁹C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," Phys. Rev. B 37, 785 (1988).

¹¹⁰ A. D. Becke, Phys. Rev. A 38, 3098 (1988); J. Chem. Phys. 98, 5648 (1993).

¹¹¹C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: The PbE₀ model," J. Chem. Phys. **110**, 6158 (1999).

¹¹²J.-D. Chai and M. Head-Gordon, "Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections," Phys. Chem. Chem. Phys. **10**, 6615 (2008).

¹¹³Y. Zhao and D. G. Truhlar, "The Mo6 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals," Theor. Chem. Acc. 120, 215 (2008).

¹¹⁴Y. Zhao and D. G. Truhlar, "A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and non-covalent interactions," J. Chem. Phys. **125**, 194101 (2006).

¹¹⁵P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, "*Ab initio* calculation of vibrational absorption and circular dichroism spectra using density functional force fields," J. Phys. Chem. **98**, 11623 (1994).

¹¹⁶D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, "Energyadjusted *ab initio* pseudopotentials for the second and third row transition elements," Theor. Chim. Acta 77, 123 (1990).

¹¹⁷J. M. L. Martin and A. Sundermann, "Correlation consistent valence basis sets for use with the stuttgart-dresden-bonn relativistic effective core potentials: The atoms Ga-Kr and In-Xe," J. Chem. Phys. **114**, 3408 (2001).

¹¹⁸B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson, and T. L. Windus, "New basis set exchange: An open, up-to-date resource for the molecular sciences community," J. Chem. Inf. Model. **59**, 4814 (2019).

¹¹⁹J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett. 77, 3865 (1996).

¹²⁰F. Weigend and R. Ahlrichs, "Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy," Phys. Chem. Chem. Phys. 7, 3297 (2005).

¹²¹ R. Bauernschmitt and R. Ahlrichs, "Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory," Chem. Phys. Lett. **256**, 454 (1996).

¹²²M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, "Molecular excitation energies to high-lying bound states from time-dependent density-functional response theory: Characterization and correction of the time-dependent local density approximation ionization threshold," J. Chem. Phys. **108**, 4439 (1998).

¹²³R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, "An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules," J. Chem. Phys. **109**, 8218 (1998).

¹²⁴ M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson *et al.*, Gaussian 11, Revision H.04, Gaussian, Inc., Wallingford, CT, 2011.

¹²⁵ R. Bauernschmitt and R. Ahlrichs, "Stability analysis for solutions of the closed shell Kohn–Sham equation," J. Chem. Phys. **104**, 9047 (1996).

¹²⁶ R. Seeger and J. A. Pople, "Self-consistent molecular orbital methods. XVIII. Constraints and stability in Hartree–Fock theory," J. Chem. Phys. 66, 3045 (1977).
 ¹²⁷ H. Hratchian and H. Schlegel, *Theory and Applications of Computational Chemistry: The First 40 Years* (Dykstra, CE, 2005), p. 195.

¹²⁸H. F. Schaefer III and Y. Yamaguchi, "A new dimension to quantum chemistry: Theoretical methods for the analytic evaluation of first, second, and third derivatives of the molecular electronic energy with respect to nuclear coordinates," J. Mol. Struct.: THEOCHEM **135**, 369 (1986).

¹²⁹ R. E. Stratmann, J. C. Burant, G. E. Scuseria, and M. J. Frisch, "Improving harmonic vibrational frequencies calculations in density functional theory," J. Chem. Phys. **106**, 10175 (1997).

ARTICLE

¹³⁰F. Santoro, R. Improta, A. Lami, J. Bloino, and V. Barone, "Effective method to compute Franck-Condon integrals for optical spectra of large molecules in solution," J. Chem. Phys. **126**, 084509 (2007).

¹³¹F. Santoro, A. Lami, R. Improta, and V. Barone, "Effective method to compute vibrationally resolved optical spectra of large molecules at finite temperature in the gas phase and in solution," J. Chem. Phys. **126**, 184102 (2007).

¹³²L. M. Thompson, H. Harb, and H. P. Hratchian, "Natural ionization orbitals for interpreting electron detachment processes," J. Chem. Phys. **144**, 204117 (2016).

¹³³L. M. Thompson, C. C. Jarrold, and H. P. Hratchian, "Explaining the MoVo⁻₄ photoelectron spectrum: Rationalization of geometric and electronic structure," J. Chem. Phys. **146**, 104301 (2017).

¹³⁴J. A. DeVine, M. L. Weichman, B. Laws, J. Chang, M. C. Babin, G. Balerdi, C. Xie, C. L. Malbon, W. C. Lineberger, D. R. Yarkony, R. W. Field, S. T. Gibson, J. Ma, H. Guo, and D. M. Neumark, "Encoding of vinylidene isomerization in its anion photoelectron spectrum," *Science* **358**, 336 (2017).

¹³⁵M. C. Babin, J. A. DeVine, M. DeWitt, J. F. Stanton, and D. M. Neumark, "High-resolution photoelectron spectroscopy of cryogenically cooled NO₃⁻," J. Phys. Chem. Lett. **11**, 395 (2020).

¹³⁶J. Zhou, E. Garand, and D. M. Neumark, "Slow electron velocity-map imaging spectroscopy of the C_4H^- and C_4D^- anions," J. Chem. Phys. **127**, 154320 (2007).

¹³⁷M. L. Weichman, L. Cheng, J. B. Kim, J. F. Stanton, and D. M. Neumark, "Lowlying vibronic level structure of the ground state of the methoxy radical: Slow electron velocity-map imaging (SEVI) spectra and Köppel-Domcke-Cederbaum (KDC) vibronic Hamiltonian calculations," J. Chem. Phys. **146**, 224309 (2017).

¹³⁸Y. J. Ko, H. Wang, R. Cao, D. Radisic, S. N. Eustis, S. T. Stokes, S. Lyapustina, S. X. Tian, and K. H. Bowen, "Photoelectron spectroscopy of homogeneous nucleic acid base dimer anions," Phys. Chem. Chem. Phys. **12**, 3535 (2010).

¹³⁹S. J. Kregel, G. K. Thurston, and E. Garand, "Photoelectron spectroscopy of anthracene and fluoranthene radical anions," J. Chem. Phys. **148**, 234306 (2018).

¹⁴⁰C. G. Bailey, C. E. H. Dessent, M. A. Johnson, and K. H. Bowen, "Vibronic effects in the photon energy-dependent photoelectron spectra of the CH_3CN^- dipole-bound anion," J. Chem. Phys. **104**, 6976 (1996).

¹⁴¹K. M. Ervin and W. C. Lineberger, "Photoelectron spectra of dicarbon(1-) and ethynyl(1-)," J. Phys. Chem. **95**, 1167 (1991).

¹⁴²C. E. Cleeton and N. H. Williams, "Electromagnetic waves of 1.1 cm wave-length and the absorption spectrum of ammonia," Phys. Rev. 45, 234 (1934).

¹⁴³A. M. Oliveira, Y.-J. Lu, J. H. Lehman, P. B. Changala, J. H. Baraban, J. F. Stanton, and W. C. Lineberger, "Photoelectron spectroscopy of the methide anion: Electron affinities of $^{\circ}$ Ch₃ and $^{\circ}$ Cd₃ and inversion splittings of Ch₃⁻ and Cd₃⁻," J. Am. Chem. Soc. **137**, 12939 (2015).

¹⁴⁴M. L. Weichman, J. B. Kim, and D. M. Neumark, "Rovibronic structure in slow photoelectron velocity-map imaging spectroscopy of CH₂CN⁻ and CD₂CN⁻," J. Chem. Phys. **140**, 104305 (2014).

¹⁴⁵M. A. Duncan, "Invited review article: Laser vaporization cluster sources," Rev. Sci. Instrum. **83**, 041101 (2012).

¹⁴⁶CRC Handbook of Chemistry and Physics, 81st ed., edited by D. R. Lide (CRC Press, 2000).

¹⁴⁷C. P. Harrilal, A. F. DeBlase, J. L. Fischer, J. T. Lawler, S. A. McLuckey, and T. S. Zwier, "Infrared population transfer spectroscopy of cryo-cooled ions: Quantitative tests of the effects of collisional cooling on the room temperature conformer populations," J. Phys. Chem. A **122**, 2096 (2018).

populations," J. Phys. Chem. A **122**, 2096 (2018). ¹⁴⁸L. Voronina and T. R. Rizzo, "Spectroscopic studies of kinetically trapped conformations in the gas phase: The case of triply protonated bradykinin," Phys. Chem. Chem. Phys. **17**, 25828 (2015).

 149 J. A. DeVine, M. C. Babin, and D. M. Neumark, "Photoelectron spectra of $\rm Al_2O_2^-$ and $\rm Al_3O_3^-$ via slow electron velocity-map imaging," Faraday Discuss. 217, 235 (2019).

¹⁵⁰M. C. Babin, M. DeWitt, M. L. Weichman, J. A. DeVine, and D. M. Neumark, "High-resolution anion photoelectron spectroscopy of cryogenically cooled 4atom silicon carbides," Mol. Phys. 2020, 1.

¹⁵¹M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis, and E. Giamello, "Photoformation and structure of oxygen anion radicals (O_2^-) and nitrogen-containing anion radicals adsorbed on highly dispersed titanium oxide anchored onto porous Vycor glass," J. Phys. Chem. **89**, 5689 (1985).

¹⁵²J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, and D. W. Bahnemann, "Understanding TiO₂ photocatalysis: Mechanisms and materials," Chem. Rev. **114**, 9919 (2014).