Structural Isomers of Ti$_2$O$_4$ and Zr$_2$O$_4$ Anions Identified by Slow Photoelectron Velocity-Map Imaging Spectroscopy

Jongjin B. Kim, Marissa L. Weichman, and Daniel M. Neumark*

Department of Chemistry, University of California, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: High-resolution anion photoelectron spectra are reported for the group 4 metal dioxide clusters Ti$_2$O$_4^-$ and Zr$_2$O$_4^-$. Slow photoelectron velocity-map imaging (SEVI) spectroscopy of cryogenically cooled, mass-selected anions yields photoelectron spectra with submillielectronvolt resolution, revealing extensive and well-resolved vibrational progressions. By comparison of the spectra with Franck-Condon simulations, we have identified the C$_{2v}$ and C$_{3v}$ isomers as the ground states of Ti$_2$O$_4^-$ and Zr$_2$O$_4^-$ anions, respectively. Minor contributions from the C$_{3h}$ isomer of Ti$_2$O$_4^-$ and the C$_{5v}$ isomer of Zr$_2$O$_4^-$ are also seen. The SEVI spectra yield upper bounds for the adiabatic detachment energies, as well as vibrational frequencies for various modes of the neutral Ti$_2$O$_4$ and Zr$_2$O$_4$ species.

1. INTRODUCTION

Titanium oxide and zirconium oxide are technologically important materials, with wide applications in pigments, refractory ceramics, catalysis, and photochemistry. Although the surface chemistry of the bulk oxide materials has been extensively studied, a considerable effort has also been made in understanding the structure and reactivity of small metal oxide clusters, including (MO$_2$)$_n$ (M = Ti, Zr) clusters. Point defects in bulk materials can be important catalytically active sites, and isolated gas-phase clusters can be used as structural and reactive analogues that are more tractable for detailed study. Transition metal oxide clusters exhibit different structural motifs than those found in the bulk material, and attempts have been made to predict and observe the relevant sizes and the consequences of these motifs for their reactive chemistry. Spectroscopic characterization of polymetal oxide clusters has proved challenging, although some of these species have been investigated by matrix isolation infrared spectroscopy, photoelectron (PE) spectroscopy, and infrared photodissociation (IRPD) spectroscopy. Compared to the other methods, photoelectron spectroscopy is perhaps the most general but its resolution is typically lower; in particular, vibrational structure is often not resolved for metal oxide clusters. We report the first high-resolution photoelectron spectra of anionic polynuclear transition metal oxides by combining cryogenic ion cooling with slow electron velocity-map imaging, yielding extensive and well-resolved vibrational progressions. By comparing the experimental and calculated spectra, we identify the most stable gas-phase M$_2$O$_4^-$ isomers as well as the next most stable isomers.

Bulk titania and zirconia have large bandgaps due to fully oxidized metal centers and are both formally d$^0$ systems, but they adopt different structures. While ZrO$_2$ has a single monoclinic crystal form at ambient conditions, TiO$_2$ is found naturally in anatase, rutile, and brookite forms. Metal oxide clusters can have dramatically different structures than those found in the bulk material, and the transition between the two regimes is not well-understood. Moreover, titanium and zirconium oxide clusters show strong size-dependent reactivity with various molecules of catalytic interest, suggesting that an understanding of cluster properties may lead to a better understanding of what controls their reactivity. It is therefore of considerable interest to track the evolution of metal oxide structures with cluster size.

Several spectroscopic methods have been applied to titanium and zirconium oxide clusters. Photoionization mass spectrometry showed that, in the presence of oxygen, the most stable neutral clusters have M$_2$O$_{2n}$ and M$_2$O$_{2n+1}$ composition. IR resonance-enhanced multiphoton ionization spectroscopy yielded IR spectra of neutral titanium and zirconium oxide clusters. The observed cluster compositions were generally deficient in oxygen, likely due to less-oxidized clusters possessing a lower ionization potential, and only broad vibrational features were resolved. Anion PE spectra have been obtained for titanium oxide anion clusters with an emphasis on determining the electron affinity and band gap of (TiO$_2$)$_n$ as a function of cluster size for $n = 1$–10; this latter property is one of the key characteristics determining the photochemistry of bulk TiO$_2$.

More detailed spectroscopy has been performed on specific (MO$_2$)$_n$ clusters. The vibronic structure and geometries of triatomic TiO$_2$ and ZrO$_2$ have been characterized by a variety of techniques. However, less is known about the next smallest (MO$_2$)$_3$ clusters. The M$_2$O$_4$ clusters have been isolated in an inert gas matrix and well-resolved IR vibrational spectra have been obtained of those species. Anion PE spectra have been reported for Ti$_2$O$_4^-$, but the electron kinetic energy clusters can have dramatically different structures than those found in the bulk material, and the transition between the two regimes is not well-understood. Moreover, titanium and zirconium oxide clusters show strong size-dependent reactivity with various molecules of catalytic interest, suggesting that an understanding of cluster properties may lead to a better understanding of what controls their reactivity. It is therefore of considerable interest to track the evolution of metal oxide structures with cluster size.

Several spectroscopic methods have been applied to titanium and zirconium oxide clusters. Photoionization mass spectrometry showed that, in the presence of oxygen, the most stable neutral clusters have M$_2$O$_{2n}$ and M$_2$O$_{2n+1}$ composition. IR resonance-enhanced multiphoton ionization spectroscopy yielded IR spectra of neutral titanium and zirconium oxide clusters. The observed cluster compositions were generally deficient in oxygen, likely due to less-oxidized clusters possessing a lower ionization potential, and only broad vibrational features were resolved. Anion PE spectra have been obtained for titanium oxide anion clusters with an emphasis on determining the electron affinity and band gap of (TiO$_2$)$_n$ as a function of cluster size for $n = 1$–10; this latter property is one of the key characteristics determining the photochemistry of bulk TiO$_2$.

More detailed spectroscopy has been performed on specific (MO$_2$)$_n$ clusters. The vibronic structure and geometries of triatomic TiO$_2$ and ZrO$_2$ have been characterized by a variety of techniques. However, less is known about the next smallest (MO$_2$)$_3$ clusters. The M$_2$O$_4$ clusters have been isolated in an inert gas matrix and well-resolved IR vibrational spectra have been obtained of those species. Anion PE spectra have been reported for Ti$_2$O$_4^-$, but the electron kinetic energy
resolution of 30 meV was insufficient to resolve any vibrational structure.\textsuperscript{28,29}  

These experiments require comparison with theory for their interpretation. Titanium oxide cluster geometries have been determined by Hartree–Fock theory,\textsuperscript{37} various density functional methods,\textsuperscript{38–41} simulated annealing methods refined by density functional theory,\textsuperscript{42,43} an evolutionary algorithm,\textsuperscript{44} and coupled-cluster theory.\textsuperscript{45} Similarly, structures of zirconium oxide clusters have been calculated by density functional theory (DFT),\textsuperscript{26,46} an evolutionary algorithm to find the global minimum,\textsuperscript{47} and coupled-cluster theory.\textsuperscript{48} Calculations agree with experiments on the structures and energies of the MO\textsubscript{2} triatomic species, but there is more uncertainty on the n = 2 clusters. Electronic structure calculations indicate that the lowest energy structures for the neutral and anionic clusters are C\textsubscript{2v}, C\textsubscript{2h}, or C\textsubscript{3v} isomers (Figure 1).\textsuperscript{37,38,40,45,47,48} with either two or three oxygen atoms bridging the metal atoms. Other structures have been considered, but they are consistently found to be higher in energy and are not considered in this work.\textsuperscript{40,45,47} While calculations have agreed upon the C\textsubscript{2v} isomer as the stable neutral form of Ti\textsubscript{2}O\textsubscript{4} in agreement with the matrix isolation IR study,\textsuperscript{36} there is more disagreement about the structure of the anions. Different methods have variously identified all three isomers as the most stable forms of Ti\textsubscript{2}O\textsubscript{4} – and Zr\textsubscript{2}O\textsubscript{4} –.\textsuperscript{38,40,45,48} Zhai and Wang\textsuperscript{29} assigned the ground state of Ti\textsubscript{2}O\textsubscript{4} – to the C\textsubscript{3v} isomer by comparing experimental and calculated vertical detachment energies.

The highest level calculations to date, at a coupled-cluster level and complete basis set extrapolation [CCSD(T)/CBS, were carried out by Li and Dixon.\textsuperscript{45,48} They found the C\textsubscript{3v} and C\textsubscript{2v} isomers of Ti\textsubscript{2}O\textsubscript{4} – and Zr\textsubscript{2}O\textsubscript{4} –, respectively, to be the most stable, but the other isomers are very close in energy. Moreover, their calculated Ti\textsubscript{2}O\textsubscript{4} – detachment energies for all isomers were compatible with the experimental PE results. The authors noted that, to make a definitive assignment of anion isomerism with PE spectroscopy, vibrational resolution and a comparison with Franck–Condon (FC) simulations are necessary. These calculations thus imply that probing the M\textsubscript{2}O\textsubscript{4} – species with a high-resolution anion PE technique could definitively resolve the question of which isomers are present.

In this work, we report slow electron velocity-map imaging (SEVI) spectra of cryogenically cooled Ti\textsubscript{2}O\textsubscript{4} – and Zr\textsubscript{2}O\textsubscript{4} –. This combination of techniques results in PE spectra with submillielectronvolt resolution, yielding well-resolved progressions in low-frequency vibrational modes for both species. By comparing the experimental results with Franck–Condon simulations and calculated vibrational frequencies, we reassign the dominant feature in the Ti\textsubscript{2}O\textsubscript{4} – PE spectra to the C\textsubscript{2v} isomer and identify a weak contribution from the C\textsubscript{2h} isomer. The lowest-energy isomer of Zr\textsubscript{2}O\textsubscript{4} – is the C\textsubscript{3v} isomer, but a small amount of the C\textsubscript{2v} isomer is present. Vibrational frequencies of various modes are also assigned for the neutral M\textsubscript{2}O\textsubscript{4} species.

2. EXPERIMENTAL SECTION

All experimental spectra were obtained with our high-resolution SEVI anion photoelectron spectrometer, the details of which have been described previously.\textsuperscript{49–51} Anion metal oxide species are created in a laser ablation source, stored and cooled in a cryogenic ion trap, extracted into a time-of-flight mass spectrometer, and photodetached with a tunable laser. SEVI uses comparatively low extraction voltages on a velocity-map imaging (VMI) electron spectrometer,\textsuperscript{52} allowing for high-resolution photoelectron spectra at low electron kinetic energies. Titanium and zirconium oxide dimer anions were produced by laser ablation of a titanium or zirconium solid sample quenched by a pulse of helium gas. There were sufficient residual oxides in the metal and contaminant oxygen in the gas line for production of metal oxide ions. The ions were stored in an octopole ion trap held at 5 K and cooled by cryogenic buffer gas for 40 ms. A 20:80 mix of H\textsubscript{2}/He was used to cool the Zr\textsubscript{2}O\textsubscript{4} – ions, conditions which have cooled ions down to 10 K.\textsuperscript{51} We have previously found that including H\textsubscript{2} in the buffer gas enhances vibrational cooling of anions.\textsuperscript{53} However, Ti\textsubscript{2}O\textsubscript{4} – reacts with H\textsubscript{2} to form a Ti\textsubscript{2}O\textsubscript{4}H\textsubscript{2} product, so the Ti\textsubscript{2}O\textsubscript{4} – ions were cooled with only helium as a buffer gas, possibly resulting in less efficient cooling.

After storage and cooling, the ions were extracted into a time-of-flight mass spectrometer and focused to the interaction region of a VMI spectrometer. The ion packets of the most abundant isotopologues, \textsuperscript{49}Ti\textsubscript{16}O\textsubscript{4} – and \textsuperscript{93}Zr\textsubscript{16}O\textsubscript{4} –, were then photodetached with the output of a Nd:YAG-pumped tunable dye laser. The VMI electrostatic lens focused the photoelectrons to an imaging detector. The resulting 2D projection was used to reconstruct the 3D radial and angular velocity distribution by the maximum-entropy method MEVELEER developed recently by Dick.\textsuperscript{54}

The radial distribution gives the electron velocity and hence the electron kinetic energy (eKE) distribution. The best resolution of a VMI spectrometer is obtained at lowest kinetic energy; SEVI uses low extraction potentials to expand the image of the low-eKE, high-resolution components of a given photoelectron image, yielding spectra with submillielectronvolt resolution. To obtain a full set of high-resolution spectra, the laser wavelength was tuned in energy so that high-resolution spectra could be obtained for each region of interest. As intensities near threshold may depend on threshold partial-wave contributions,\textsuperscript{55} the spectra were then scaled in intensity to the appropriate low-resolution overview spectrum and then combined. Each spectrum is plotted as a function of electron binding energy (eBE), given by eBE = hν – eKE, where hν is the photon energy used in that particular spectrum.

The photoelectron image also yields the photoelectron angular distribution (PAD). For photodetachment with linearly polarized light as in this experiment, the PAD is given by

\[
\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{tot}}}{4\pi} \left[ 1 + \beta \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \right]
\]

where θ is the angle relative to the axis of polarization. The anisotropy parameter β varies from −1 to 2, giving the limits of a PAD perpendicular and parallel to the polarization axis.\textsuperscript{56,57} As the value of β for a given transition varies with eKE, quantitative values are not reported here; the PAD is used mainly as a qualitative guide to distinguish between different electronic transitions.

3. THEORETICAL METHODS

Li and Dixon\textsuperscript{45,48} calculated the energetics of the M\textsubscript{2}O\textsubscript{4} anionic and neutral isomers at a benchmark CCSD(T)/CBS level. To compare their results with the experimental anion PE spectra of Ti\textsubscript{2}O\textsubscript{4} –, they generated FC spectra for photodetachment from all three isomers at a...
less costly BP86/aug-cc-pVDZ-PP level. In order to account for typical experimental conditions in PE spectroscopy, they presented FC spectra with an ion vibrational temperature of 300 K and an instrumental resolution full width at half-maximum (fwhm) of 50 meV. Under these conditions, individual vibronic transitions are not resolved and only overall band profiles are distinguished. Although there were no experimental Zr2O4− spectra for comparison, they simulated FC spectra at the same level. In anticipation of higher-resolution techniques, they also simulated spectra with 1 meV resolution but still at a vibrational temperature of 300 K. SEVI with ion trapping and cooling, however, allows for submillielectronvolt resolution and vibrationally cold ions. Hence, for comparison with our experiments, we performed an independent set of electronic structure calculations and FC simulations assuming no anion vibrational excitation.

The work by Li and Dixon also found that the BP86 density functional gave qualitatively similar geometries and energies compared to CCSD(T). Consequently, geometries and harmonic vibrational frequencies were determined with the BP86 functional. As with our previous study of group 4 triatomic metal dioxides, the LANL2TZ basis set and the Hay-Wadt effective core potential were used for metal atoms, while the 6-311+G* basis set was used for oxygen atoms. Electronic structure calculations, geometry optimizations, and vibrational analyses were all performed with Q-Chem 4.0.

Franck–Condon simulations for the photodetachment spectra were made with the ezSpectrum program in the harmonic approximation but with Duschinsky mixing of all modes. The experimental spectra have been obtained at differing resolution depending on the chosen photon energies. Therefore, the simulated spectra have been convolved with Gaussian distributions of different widths (15, 60, and 100 cm−1 fwhm) to facilitate comparison with experimental spectra.

4. RESULTS

4.1. Experiment. Photoelectron spectra of Ti2O4− and Zr2O4− are shown in Figures 2–5. Overview spectra of Ti2O4− are displayed in Figure 2, while higher-resolution spectra are shown in Figures 3 and 4, highlighting structure at eBEs between 14 000 and 17 000 cm−1 and between 16 500 and 17 800 cm−1, respectively. The overview and high-resolution spectra of Zr2O4− are shown in Figure 5.

Owing to the dependence of energy resolution on eKE in the SEVI electron spectrometer, overview spectra for Ti2O4− are displayed at three different energies to highlight structure in different energy regions, from 14 500 to 21 000 cm−1. There is a weak but extended progression of peaks beginning from ~14 000 to 17 000 cm−1 (band A) that is then subsumed by a stronger spectral feature (band B). The high-resolution spectra encompassing band A (Figure 3) exhibit a main progression comprising peaks A1–A16, with a typical peak spacing of ~180 cm−1. A second progression of peaks a5–a12 is visible with much smaller intensity. It has the same peak spacing as the main progression but is offset ~80 cm−1 higher. The three different traces in Figure 3 illustrate that the relative intensities of peaks drop dramatically at low eKE (i.e., at eBE close to the photon energy), where the resolution is highest. To maintain a balance between signal and resolution, the peak assignments are taken from spectra with eKE ~500 cm−1, giving typical peak widths of 15 cm−1 fwhm in this region.
The overview spectra also show much stronger photoelectron signal at higher eBE, ~17 000–20 000 cm\(^{-1}\) (band B). Much of the signal is not fully resolved, but two peak progressions are visible with a spacing of 95 cm\(^{-1}\), one from ~17 000 to 18 000 cm\(^{-1}\) and another from ~18 500 to 19 500 cm\(^{-1}\). As the region in the higher-eBE progression is highly congested, high-resolution spectra were obtained only for the low-eBE portion of band B (Figure 4). The progression observed in the overview spectra is still the dominant feature, comprising peaks B1–B15 with a typical peak spacing of 95 cm\(^{-1}\). Peak intensities do not disappear near threshold, resulting in peak widths as narrow as 7 cm\(^{-1}\) at eKEs around 30 cm\(^{-1}\). Weak features other than the main B1–B15 progression are also visible above 17 300 cm\(^{-1}\), though poor signal-to-noise and spectral congestion prevents clear peak labeling or assignments.

Peak positions, PADs, and assignments for Ti\(_2\)O\(_4\)\(^−\) high-resolution SEVI spectra are listed in Table S1 in Supporting Information. The value of \(\beta\) describing the PAD is a function of eKE, which is not a constant for a given transition in this experiment. At large eKE (1000–4000 cm\(^{-1}\)), the anisotropy parameter of all transitions is unambiguously positive (\(\beta > 0.6\)), but at eKE < 500 cm\(^{-1}\), the value of \(\beta\) for a given well-resolved peak can be binned as either 0 < \(\beta\) < 0.2 or 0.3 < \(\beta\) < 1 (Figure S1, Supporting Information). These two categories are labeled a- and b-PADs. The PAD is characterized by a \(\beta\)-value of a for peaks B8–B15, while peaks A3–A14 and a8–a12 had a b-PAD. All other peaks had too little signal for an accurate determination.

In contrast to the extended progressions seen in the Ti\(_2\)O\(_4\)\(^−\) spectra, the Zr\(_2\)O\(_4\)\(^−\) spectra show a strong onset (peak A) and no immediately dominant peak progression, though there are several peaks with strong intensity (Figure 5). Significant structure extends for only ~2000 cm\(^{-1}\) beyond the band onset, and peak widths as narrow as 4 cm\(^{-1}\) are obtained. A very weak progression is also present close to the band onset (Figure 5 inset), comprising peaks a1–a7, with a typical peak spacing of 95 cm\(^{-1}\). In contrast with all other assigned peaks, for which the PAD is b, these have an a-PAD. Peak positions, PADs, and assignments for Zr\(_2\)O\(_4\)\(^−\) spectra are listed in Table S2 in Supporting Information.

4.2. Calculations. Calculated relative energies for anionic and neutral isomers of Ti\(_2\)O\(_4\) and Zr\(_2\)O\(_4\) are summarized in Table 1. Adiabatic detachment energies (ADE), vertical detachment energies (VDE), and reorganization energies are also listed. These values are defined as the difference between anion and neutral energies at their respective minima, the difference at anion geometries, or the difference between VDE and ADE, respectively. These values are taken from the benchmark CCSD(T)/CBS calculations by Li and Dixon,\(^{45,48}\) who found that the different isomers are only a few kilocalories per mole apart in energy. This difference is smaller than the expected error of BP86 and other density functionals,\(^{62}\) hence the values from their papers are used here rather than

Figure 4. SEVI spectra of the low-eBE portion of the C\(_2\)v Ti\(_2\)O\(_4\) PE spectrum (band B). The overview spectrum (blue, at photon energy of 17 824 cm\(^{-1}\)) is offset vertically from the high-resolution segments (black).

Figure 5. SEVI spectra of Zr\(_2\)O\(_4\). The overview spectrum (blue, at photon energy of 17 682 cm\(^{-1}\)) is offset vertically from the high-resolution segments (black). (Inset) Weak but reproducible peaks between 15 000 and 15 700 cm\(^{-1}\).
The all anions have a singly occupied molecular orbital (SOMO) of the totally symmetric representation of the respective point group. The anion SOMO and major geometry changes are shown in Figure 6.

Franck–Condon simulations are shown in Figure 7 for photodetachment of all three isomers of Ti$_2$O$_4$$^-$ and Zr$_2$O$_4$$^-$. Each of the three isomers has a distinct FC profile, which changes somewhat depending on the metal atom. The C$_{2h}$ isomer exhibits an extended progression in the lowest-frequency totally symmetric mode, the $\nu_4$ mode. The predicted peak spacing is 200 and 159 cm$^{-1}$ for Ti and Zr, respectively. The band progression is calculated to extend 6000 cm$^{-1}$ for Ti$_2$O$_4$ but only 1500 cm$^{-1}$ for Zr$_2$O$_4$. The C$_{3v}$ isomer also has a large progression in its lowest-frequency totally symmetric mode, the $\nu_5$ mode, with a predicted peak spacing of 94 and 97 cm$^{-1}$ for Ti and Zr. However, other modes are also predicted to be FC-active, especially the $\nu_3$ mode, resulting in a highly congested spectrum starting from ~1500 cm$^{-1}$ above the vibrational origin and extending at least 6000 cm$^{-1}$. Displacement vectors for the most FC-active C$_{2h}$ and C$_{3v}$ modes are illustrated in Figure 6.

In contrast, the FC simulation of the C$_{3v}$ isomer is not dominated by activity in any one particular mode. The vibrational origin is strong, and appreciable FC activity is predicted in all the totally symmetric modes (with the exception of $\nu_3$ in Ti$_2$O$_4$). There is also some minor even quanta excitation in the nontotally symmetric $\nu_6$ mode, which corresponds to the terminal oxygen wagging motion, owing to the large change in vibrational frequency between anion and neutral species (Table S5, Supporting Information).

It is also of interest to consider the infrared spectra of the various anion and neutral isomers. For this purpose, simulated vibrational spectra are displayed in Figure S2 (Supporting Information).

## 5. ANALYSIS

### 5.1. Assignment of Ti$_2$O$_4$$^-$ Spectra

Bands A and B have different PADs, suggesting that they correspond to two different photodetachment transitions rather than two vibrational progressions within the same electronic transition. Different experimental conditions at identical photodetachment energies can also change the relative intensities of the two bands (Figure S3, Supporting Information), though the correlation between conditions used and band strengths is...
not clear. The two bands have peak progressions with different spacings, ruling out detachment from two anion states to the same neutral state. While they could arise from photodetachment to two close-lying neutral states from the same anion state, theoretical calculations do not support the existence of very low-lying states for any of the neutral isomers, all of which are closed-shell species. The two bands are most reasonably assigned to photodetachment from two different anion isomers, each going to a neutral isomer of the same molecular symmetry and overall structure.

The two bands can be assigned by comparing the observed peak spacings and intensity distributions to calculations. Band A exhibits an extended progression in a vibrational mode with a frequency of \( \sim 180 \text{ cm}^{-1} \), while the clearest progression in band B involves a mode with a frequency of \( \sim 95 \text{ cm}^{-1} \). These correspond well to the calculated frequencies of \( \nu_4 \) mode of neutral \( C_{2h} \) isomer (200 cm\(^{-1}\) ) and \( \nu_5 \) mode of \( C_{2v} \) isomer (94 cm\(^{-1}\)) (see Table 1). By comparison, the \( \nu_4 \) modes of \( C_{2v} \) and \( C_{3v} \) isomers have calculated frequencies of 315 and 400 cm\(^{-1}\) respectively, and do not match the observed vibrational spacing. While \( \Delta \nu = \) even transitions are possible for nontotally symmetric modes, such progressions are often weak; the large FC activity is indicative of strong activity in fully FC-allowed modes. The vibrational spacing is consistent with bands A and B corresponding to photodetachment of \( C_{2h} \) and \( C_{2v} \) isomers, respectively, of \( \text{Ti}_2\text{O}_4^- \).

The FC simulations in Figure 7 confirm this assignment. The \( C_{2h} \) \( \nu_4 \) and \( C_{2v} \) \( \nu_5 \) modes are calculated to be the most FC-active modes for the respective isomers, matching the assigned vibrational activity on the basis of peak spacing. The FC envelopes for both isomers are \( >4000 \text{ cm}^{-1} \) wide, consistent with the observation that both bands are extended \( >3000 \text{ cm}^{-1} \).

There is also significant simulated FC activity in other modes of the \( C_{2v} \) isomer. Due to overlapping contributions from multiple modes, this activity appears as a bimodal distribution with peak spacing approximating that of the \( \nu_5 \) frequency, as seen in the red and blue traces in the \( C_{2v} \) simulation in Figure 7. This bimodal appearance is also seen in the experimental spectra, most clearly in the black and red traces in Figure 2. The \( C_{3v} \) simulation, in contrast, has a strong vibrational onset and FC activity is more distributed among the various FC-active modes, completely unlike that observed for bands A and B. The much stronger signal associated with band B suggests that the \( C_{2v} \) anion isomer is more stable than the \( C_{2h} \) isomer, a point discussed further in section 6.1.

The eKE-dependent intensities in bands A and B, most apparent in Figures 3 and 4, are also consistent with this assignment. The peak intensities at low eKE drop off for the

![Figure 7. Franck–Condon simulations of photodetachment of \( M_2O_4^- \) for \( C_{2h} \), \( C_{2v} \), and \( C_{3v} \) isomers with \( M = \text{Ti, Zr} \). Simulations are offset vertically and broadened by Gaussian distributions with fwhm of (black) 15, (red) 60, and (blue) 100 cm\(^{-1}\).](dx.doi.org/10.1021/ja502713v)
peaks in band A but not in band B. These results can be understood with reference to the Wigner threshold law as applied to the photodetachment cross section \( \sigma \) for low-energy electrons, \( \sigma \propto (eKE)^{1/4} \), where \( I \) is the orbital angular momentum of the outgoing electron.

Our results imply that the partial waves contributing to photodetachment near threshold differ for the two bands, with more s-wave \((I = 0)\) detachment for band B and more p-wave \((I = 1)\) or higher-order detachment for band A. The SOMO shown in Figure 6 for the \( C_{2h} \) isomer has \( g \) symmetry with respect to inversion through the center of symmetry. As shown by Reed et al., \(^63\) s-wave photodetachment from such an orbital is symmetry-forbidden, resulting in eKE-dependent intensities of the type seen in band A. The \( C_{2v} \) isomer has no center of symmetry, so this selection rule does not apply, and s-wave detachment is fully allowed.

As the \( C_{2v} \) and \( C_{2h} \) isomers are only a few kilocalories per mole apart in energy while the vibrational progressions are highly extended, it is worth considering whether any spectral features can be attributed to isomerization. However, B3LYP calculations show that the barrier to isomerization along the oxygen wagging motion connecting those isomers is at least 0.70 eV. \(^64\) While higher-eBE portions of the spectra may well have contributions from motion near the barrier, the assigned features at lower eBE can be attributed solely to one isomer or the other.

Although the experimental data for the \( Ti_2O_4^- \) SEVI spectra are consistent with the lower-resolution PE spectrum reported by Zhai and Wang, \(^29\) we assign the main feature to the \( C_{2v} \) isomer while they assigned it to the \( C_{2h} \) isomer. The previous PE study had no vibrationally resolved structure, so the assignments were made by comparison of the experimental electronic state energies to those obtained by theoretical calculations, \(^6\), \(^9\), \(^41\) which had predicted a \( C_{2v} \) anion minimum.

The calculations used, however, were made with a relatively low-level local DFT method and a plane-wave basis set. \(^38\) Subsequent DFT calculations have found either a \( C_{2h} \) or \( C_{2v} \) isomer to be the \( Ti_2O_4^- \) minimum. \(^40\), \(^45\)

In addition to enabling identification of the anion isomers, the well-resolved vibrational structure allows us to determine vibrational frequencies of the neutral \( C_{2v} \) and \( C_{2h} \) isomers of \( Ti_2O_4 \). The primary structure in band A corresponds to a progression in the \( \nu_4 \) mode in \( C_{2v} Ti_2O_4^- \) with a vibrational frequency of \( ~180 \text{ cm}^{-1} \). By fitting the \( A1 \rightarrow A16 \) progression to the lowest-order anharmonic oscillator and assuming \( \nu_4 \) corresponds to the vibrational origin, we obtain a \( \nu_4 \) fundamental of \( 185(4) \text{ cm}^{-1} \) and harmonic frequency \( \omega_{4h} = 186(4) \text{ cm}^{-1} \). If \( \omega_5 \) is not the origin, the frequencies will be slightly larger due to the anharmonicity. The \( a5 \rightarrow a12 \) progression corresponds to another progression in the same \( \nu_4 \) mode but with one quantum in another totally symmetric mode. The onset of this progression is even more difficult to determine than that of the \( A1 \rightarrow A16 \) progression due to the weak signal. If peak \( a5 \) is offset from peaks \( A1, A2, A3, \) or \( A4 \) by one quantum in a different mode, the fundamental of that mode would be \( 823, 637, 455, \) or \( 271 \text{ cm}^{-1} \), respectively. When these values are compared to the calculated frequencies of the totally symmetric modes, the best agreement comes with \( 455 \text{ cm}^{-1} \) for the \( \nu_4 \) mode. Peaks \( a5 \rightarrow a12 \) are then assigned to the \( 3_1^1 4_0^0 \) progression; a similar analysis for the \( 4_0^2 \) progression gives \( \nu_5 = 458(5) \text{ cm}^{-1} \).

The resolved vibrational structure in the \( C_{2v} \) band is dominated by the \( \sim 95 \text{ cm}^{-1} S^0_2 \) progression. Although the origin is similarly not well-established, there is much less anharmonicity compared to the \( C_{2h} 4_0^2 \) progression. By similar fitting, we obtain both the vibrational fundamental and harmonic frequencies \( \nu_4 = \omega_{4h} = 95(2) \text{ cm}^{-1} \). Note that in the high-resolution SEVI spectra, the intensities of this progression do not increase smoothly, which may be due to contributions from unresolved additional structure. However, no other evidence of such structure is seen even at a resolution of \( ~7 \text{ cm}^{-1} \).

5.2. Assignment of \( Zr_2O_4^- \) Spectra. The SEVI spectra of \( Zr_2O_4^- \) also show two overlapped bands, one considerably more intense than the other, with differing PADS and characteristic peak spacings. The same reasoning that was applied to \( Ti_2O_4^- \) suggests that these bands correspond to transitions originating from two anion isomers. As with \( Ti_2O_4^- \), the vibrational structure in the SEVI spectra readily allows us to assign each band to a particular isomer. The main band, peaks A–M, is not dominated by a single peak progression and has a strong vibrational origin, consistent with the FC simulation for photodetachment from the \( C_{2v} \) isomer. Moreover, within 1000 \text{ cm}^{-1} of the vibrational origin, significant peaks are predicted for the \( 80 \nu_1 4_0^0 2_1^1 2_1^0 \) and \( 1_3^0 \) transitions at 100, 29, 506, 740, and 856 \text{ cm}^{-1} \) above the origin. These predictions are in good agreement with the experimental positions and intensities of peaks B, C, E, H, and J (Table S2, Supporting Information) and are assigned, respectively. By appropriate combinations, peak D is assigned as the \( 4_0^2 8_0^2 \) transition, peak K as \( 5_0^0 \) and peak M as \( 2_1^1 4_0^0 \). The observed vibrational structure allows us to obtain numerous vibrational fundamentals of \( C_{2v} Zr_2O_4 \) (Table 2).

### Table 2. Summary of Experimental Detachment Energies of Anions and Vibrational Frequencies of Neutral M$_2$O$_4$ Isomers

<table>
<thead>
<tr>
<th>Anion</th>
<th>1907</th>
<th>7159</th>
<th>7165</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2h}$</td>
<td>Ti$_2$O$_4$</td>
<td>Zr$_2$O$_4$</td>
<td>Ti$_2$O$_4$</td>
</tr>
<tr>
<td>ADE, a eV</td>
<td>1.752(1)</td>
<td>1.8681(5)</td>
<td>1.783(2)</td>
</tr>
<tr>
<td>VDE, a eV</td>
<td>2.1(1)</td>
<td>1.92(6)</td>
<td>2.00(3)</td>
</tr>
<tr>
<td>$\nu_4$ cm$^{-1}$</td>
<td>2035(1)</td>
<td>888(2)</td>
<td>782(2)</td>
</tr>
<tr>
<td>$\nu_5$ cm$^{-1}$</td>
<td>458(5)</td>
<td>520(2)</td>
<td>313(2)</td>
</tr>
<tr>
<td>$\nu_6$ cm$^{-1}$</td>
<td>185(4)</td>
<td>95(2)</td>
<td>70(2)</td>
</tr>
</tbody>
</table>

aDE, adiabatic detachment energy; VDE, vertical detachment energy. bUpper limits.

The fundamental of the nontotally symmetric $\nu_5$ mode is not observed. However, its intermediate anharmonicity is small; that is, peak D is offset from the origin exactly as the combination of peaks B and C. We assume that the intramode anharmonicity is similarly small, and we give the fundamental frequency as half that of $2\nu_5$.

The weak band, peaks a1–a7, comprises a single \( ~95 \text{ cm}^{-1} \) progression. The appearance of this band suggests it should be assigned to photodetachment of the \( C_{2h} \) isomer, for which an extended $S_2^0$ progression with a peak spacing of \( 97 \text{ cm}^{-1} \) peak spacing is predicted. The lowest-frequency $\nu_4$ mode of \( C_{2h} \) Zr$_2$O$_4$ is calculated to have a frequency of \( 159 \text{ cm}^{-1} \) and is not likely to correspond to the observed band. The low signal of this band makes a precise determination of the $\nu_5$ frequency
more difficult, and we conservatively give a value of 95(10) cm\(^{-1}\).

5.3. Adiabatic and Vertical Detachment Energies. Adiabatic detachment energies (ADE) are experimentally given for each anion isomer by the position of the vibrational origin of the corresponding band in the SEVI spectrum. For Ti\(_2\)O\(_4\)\(^{-}\), which is the lowest energy transitions observed for bands A and B (peaks A1 and B1) occur at 1.752(1) and 2.035(1) eV, respectively. Since these bands are both quite broad, it is possible that these peaks are not the vibrational origins, in which case these energies are upper bounds for the ADEs of the C\(_{2h}\) and C\(_{3v}\) isomers of Ti\(_2\)O\(_4\)\(^{-}\). The vibrational origin of the main band (peak A) is clear and well-resolved in the SEVI spectrum of Zr\(_2\)O\(_4\)\(^{-}\), yielding an ADE of 1.8733(2) eV for the C\(_{3v}\) isomer. The weak band has peak A1 as the first resolved feature, giving an upper bound of 1.8681(5) eV for the ADE of the Zr\(_2\)O\(_4\)\(^{-}\) C\(_{3v}\) isomer. As this band is calculated to have an extended FC progression while its intensity is experimentally very small, the true ADE is likely to be smaller.

It is also useful to extract vertical detachment energies (VDE) from our spectra for comparison with calculations and lower-resolution photoelectron spectra. We take the experimental VDEs to be the center of gravity of each band. For Ti\(_2\)O\(_4\)\(^{-}\), the signal in band A diminishes close to threshold and the high-eBE portion overlaps with the much more intense band B. Hence only a rough estimate can be given of 2.1(1) eV for the VDE of band A (C\(_{3v}\)), compared to a more precise value of 2.28(3) eV for band B (C\(_{3v}\)). A similar procedure for Zr\(_2\)O\(_4\)\(^{-}\) yields VDEs of 1.92(6) and 2.00(3) eV for the C\(_{2h}\) and C\(_{3v}\) isomers, respectively. The small differences between VDEs for the various isomers is consistent with previous electronic structure calculations\(^,3,8,45,48\) and points to the difficulties of using these quantities as the sole basis for assigning features in photoelectron spectra to particular isomers.

6. DISCUSSION

6.1. Isomers and Energetics. Vibrationally resolved PE spectra obtained by SEVI show that the dominant photodetachment signal is from the C\(_{2h}\) and C\(_{3v}\) isomers of Ti\(_2\)O\(_4\)\(^{-}\) and Zr\(_2\)O\(_4\)\(^{-}\), respectively. As the detached electrons for all three isomers come from a metal-centered d-orbital SOMO (Figure 6), one can assume that the different isomers have a comparable photodetachment cross-section (so long as they are not too close to the detachment threshold) and thus that the observed photoelectron signal corresponds to the relative populations of the two isomers. The ions have been cooled in a clustering channel in the laser ablation source and then further cooled in the cryogenic ion trap. This combination is likely to favor production of the most stable anion isomers. It thus appears that the lowest-energy anion isomers are the C\(_{2h}\) structure for Ti\(_2\)O\(_4\)\(^{-}\) and the C\(_{3v}\) structure for Zr\(_2\)O\(_4\)\(^{-}\). On the basis of our assignment of the weak bands for the two clusters, the next highest energy isomers are the C\(_{2h}\) and C\(_{3v}\) structures for Ti\(_2\)O\(_4\)\(^{-}\) and Zr\(_2\)O\(_4\)\(^{-}\), respectively. This energy ordering agrees with the calculations by Li and Dixon\(^,45,48\) (see Table 1).

The weaker band is more prominent in Ti\(_2\)O\(_4\)\(^{-}\) than in Zr\(_2\)O\(_4\)\(^{-}\), suggesting a larger population for the higher energy anion isomer; this result may reflect less efficient cooling of Ti\(_2\)O\(_4\)\(^{-}\) by pure He in the ion trap\(^,30\) compared to the H\(_2\)/He mixture used for Zr\(_2\)O\(_4\)\(^{-}\). The Ti\(_2\)O\(_4\)\(^{-}\) ions appear to have minimal vibrational excitation, as no sequence or hot bands are observed, but inefficient cooling may still affect the isomer distribution prior to total quenching of vibrational energy.

Neutral Ti\(_2\)O\(_4\) and Zr\(_2\)O\(_4\) have been studied by IR spectroscopy in a rare gas matrix.\(^,36\) On the basis of the vibrational structure observed with varied amounts of \(^{18}\)O labeling, both Zr\(_2\)O\(_4\) and Ti\(_2\)O\(_4\) were determined to have a C\(_{2h}\) ground state in a matrix. For example, without isotope labeling, only a single peak was seen between 850 and 900 cm\(^{-1}\), as opposed to a doublet that would be present for C\(_{3v}\) isomers (see Figure S2 in Supporting Information). With partial isotope labeling, however, both the symmetric and antisymmetric stretch modes are observed due to the breaking of symmetry. Most theoretical calculations also predict a C\(_{3v}\) isomer for the neutral M\(_2\)O\(_4\) species. Hence, it appears that the energy ordering of the anion and neutral isomers is different, which is again consistent with electronic structure calculations.\(^,38,45,48\)

Although we can identify the most stable anion isomers based on the relative signal intensities, the two bands seen in the SEVI spectra for each species do not correspond to photodetachment to a common neutral isomer, as shown in Figure 8; the energetics here are from the calculations of Li and Dixon.\(^,45,48\)

Figure 8. Energy level diagram of the various isomers and charge states of Ti\(_2\)O\(_4\) and Zr\(_2\)O\(_4\). Energies are from CCSD(T) calculations by Li and Dixon.\(^,45,48\) The full arrow highlights the primary observed photodetachment channel in this work, while the dashed arrow is a minor component.
Figure S2 (Supporting Information), there are distinct differences in the IR spectra of the various isomers as well. Both methods could be successfully used to identify the $M_2O_3$– structures but in complementary ways. In particular, most of the major features in the IR spectra are due to various $M$–O and $M$=O stretching modes. In comparison, the main progressions in the $C_{v}$ and $C_{3h}$ SEVI spectra are due to much lower frequency terminal oxygen wagging modes that are barely active in the IR spectra, while the IR-active $M$–O and $M$=O modes only have significant activity in the SEVI spectra for the $C_{v}$ isomer. Also, gas-phase IR spectra of size-selected neutral metal oxide clusters are challenging to obtain, whereas the SEVI experiment yields these vibrational frequencies directly. Conversely, IRPD spectra are routinely obtained for anions, while SEVI can only give vibrational information on anions through the observation of hot bands.

6.2. Geometry and Franck–Condon Activity. Earlier interpretations of the PE spectra of $(TiO_2)_n$ clusters attributed the broad unresolved spectra to extended FC activity. The FC activity, in turn, was attributed to photodetachment of an electron from the localized SOMO in the anion, resulting in a large geometry change, as detachment from a delocalized orbital would perturb the geometry less.13,25 We reconsider this interpretation with information gained from the present study.

The specifics of FC activity differ for the various isomers. The $C_{2v}$ and $C_{3h}$ isomers have a structural motif with a $M_2O_2$ ring and two terminal oxygen atoms. The anion SOMO for both isomers distorts the angle of the out-of-plane terminal oxygen atoms. Since most of the electron density is out of the $M_2O_3$ plane, the resulting electrostatic repulsion with the oxygen atoms preferentially distorts the terminal oxygen atoms to be more coplanar with the $M_2O_2$ ring. Although the SOMO is nominally a nonbonding orbital, the resulting change in geometry leads to a large reorganization energy. Our calculations predict a 15.4° change in the $Ti$–$Ti$=O bond angle for the $Ti_2O_4$ $C_{2v}$ isomer, and the $C_{3h}$ isomer and $Zr_2O_4$ species have similar calculated changes in geometry (Figure 6).

The most FC-active modes should correspond to the symmetric bend of the terminal oxygen atoms, which would be $\nu_4$ mode of $C_{2v}$ isomer and $\nu_7$ mode of $C_{3h}$ isomer, with some conformation to $\nu_4$ mode as well. The $C_{3v}$ isomer, in contrast, has the additional anion electron localized on one atom. The molecular framework is more rigid near the SOMO than in the other isomers, and only minor changes in geometry are immediately obvious. The reorganization energy is consequently smaller than the other isomers, with the exception of $C_{3h}$ $Zr_2O_4$. The geometry changes are also not well-described by any one vibrational mode, and thus more if not all of the totally symmetric modes are expected to be FC-active.

Compared with the expected FC-active modes on the basis of the anion SOMO and geometry changes, the calculated FC simulations are in good agreement. The $M_2O_3$ $C_{2h}$ simulations exhibit a broad progression in the $\nu_4$ mode, the $C_{2v}$ simulations have large progressions in the $\nu_3$ and $\nu_5$ modes, and the $C_{3v}$ simulations have less FC activity overall but all the totally symmetric modes contribute. Relative to the other isomers, the vibrational origin is far more prominent in the $C_{2v}$ isomer spectra. It thus appears that charge localization cannot be used as the sole criterion for rationalizing the width of PE spectral features from unresolved vibrational activity. Calculated reorganization energies can provide guides for the width of the FC envelope, but in this case a proper vibrational analysis is required to definitively assign the PE features.

7. CONCLUSION

The structural isomers of $Ti_2O_5^-$ and $Zr_2O_5^-$ have been determined by comparing calculated vibrational frequencies and Franck–Condon profiles with high-resolution anion photoelectron spectra obtained by SEVI and cryogenic ion cooling. The ground $Ti_2O_5^-$ isomer is $C_{2v}$, and the next lowest-lying isomer is $C_{3h}$, while the neutral isomers are reversed in order of energy. In contrast, $Zr_2O_5^-$ is observed as the $C_{3v}$ isomer, with only trace quantities of the $C_{2v}$ isomer. Due to the extended vibrational progressions in $C_{2v}$ and $C_{3h}$ isomers, the ADE is definitively identified only for $C_{3v}$ $Zr_2O_5^-$, while upper bounds have been put on the $Zr_2O_5^-$ $C_{2v}$ isomer as well as the $Ti_2O_5^-$ $C_{2v}$ and $C_{3h}$ isomers. Various vibrational frequencies of the neutral species have been determined. The energy ordering of the anion isomers disagrees with some theoretical studies but bolsters the conclusions of previously reported sophisticated ab initio calculations by Li and Dixon,45,58 giving experimental evidence in favor of their calculated isomer energy ordering.

Even the relatively simple $(MO_2)_2$ species studied have multiple isomers close in energy that have proven a challenge to describe computationally. Moreover, few techniques are well-suited for experimentally determining the structures and energetics of size-selected metal oxide clusters. Anion PE spectroscopy can obtain detachment energies, which can be compared with calculations, but only in favorable circumstances. Such structures have vibrational structure been resolved and used to corroborate the assignments. The addition of SEVI and ion cooling to anion PE spectroscopy allows for vibrational resolution of many more systems, resulting in more conclusive assignments of structures, energies, and vibrational frequencies.

ASSOCIATED CONTENT

Supporting Information

Five tables and three figures showing full listing of experimental SEVI peak positions and assignments, calculated geometries and vibrational frequencies at the BP86/LANL2TZ level for all species considered, plots of $\beta$ as a function of $eKE$ and isomer, simulated IR spectra of all species, and overview spectra demonstrating that relative band intensities depend on experimental conditions and have different characteristic PADs. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
dneumark@berkeley.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the Air Force Office of Scientific Research under Grant FA9550-12-1-0160 and the Defense University Research Instrumentation Program under Grant FA9550-11-1-0330. M.L.W. thanks the National Science Foundation for a graduate research fellowship.

REFERENCES
