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# High-resolution photoelectron spectroscopy of $TiO_3H_2^-$ : Probing the $TiO_2^- + H_2O$ dissociative adduct

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Slow electron velocity-map imaging spectroscopy of cryogenically cooled  $\text{TiO}_3\text{H}_2^-$  anions is used to probe the simplest titania/water reaction,  $\text{TiO}_2^{0/-} + \text{H}_2\text{O}$ . The resultant spectra show vibrationally resolved structure assigned to detachment from the *cis*-dihydroxide  $\text{TiO}(\text{OH})_2^-$  geometry based on density functional theory calculations, demonstrating that for the reaction of the anionic  $\text{TiO}_2^$ monomer with a single water molecule, the dissociative adduct (where the water is split) is energetically preferred over a molecularly adsorbed geometry. This work represents a significant improvement in resolution over previous measurements, yielding an electron affinity of 1.2529(4) eV as well as several vibrational frequencies for neutral TiO(OH)<sub>2</sub>. The energy resolution of the current results combined with photoelectron angular distributions reveals Herzberg-Teller coupling-induced transitions to Franck-Condon forbidden vibrational levels of the neutral ground state. A comparison to the previously measured spectrum of bare TiO<sub>2</sub><sup>-</sup> indicates that reaction with water stabilizes neutral TiO<sub>2</sub> more than the anion, providing insight into the fundamental chemical interactions between titania and water. *Published by AIP Publishing*. https://doi.org/10.1063/1.5018414

#### I. INTRODUCTION

Titania (TiO<sub>2</sub>) is an inexpensive, extensively studied, and environmentally benign semiconducting material with widespread applications in photovoltaics,<sup>1–4</sup> pollution management,<sup>5</sup> chemical sensing,<sup>6,7</sup> and heterogeneous catalysis.<sup>8–10</sup> The landmark discovery of photosensitization of water on a TiO<sub>2</sub> electrode<sup>11</sup> sparked a decades-long pursuit to harness the photocatalytic properties of TiO<sub>2</sub> as a practical means of solar-powered hydrogen fuel production.<sup>12,13</sup> However, the success of this endeavor has been limited in part by a lack of the mechanistic understanding necessary to design better catalysts.<sup>14</sup> Here, we present high-resolution photoelectron spectra of the TiO<sub>3</sub>H<sub>2</sub><sup>-</sup> anion accompanied by theoretical analysis, in order to probe the nature of the interaction between TiO<sub>2</sub><sup>-</sup> and a single water molecule.

The most natural starting point for understanding water oxidation by TiO<sub>2</sub> is a consideration of how water adheres to bulk titania surfaces, an active and complex area of research.<sup>15–17</sup> The extent to which water dissociates on a TiO<sub>2</sub> surface is known to be dependent on surface structure,<sup>18</sup> with varying propensities for dissociative versus molecular adsorption for different crystal phases and planes<sup>19–24</sup> as well as a dependence on the extent of surface coverage by water.<sup>25,26</sup> While dissociation tends to play a minor role in water adsorption on stoichiometric TiO<sub>2</sub> surfaces, it is found to be strongly preferred at point defects such as steps,<sup>27</sup> edges,<sup>28,29</sup> and in particular, oxygen vacancies.<sup>30–36</sup> Thus, the conceptual key to understanding the surface chemistry of water on titania from a molecular level is the chemistry that occurs at these defect sites.

It is challenging to design a bulk experiment that is uniquely sensitive to the chemistry occurring at a specific surface defect. Defect sites typically make up a small fraction of total surface area and are difficult to reproducibly generate. Gas phase metal oxide clusters have been shown to be useful model systems for gaining mechanistic insight into complex catalytic processes, as these species show structural motifs such as dangling moieties and undercoordinated atoms that mimic the geometries at common defect sites.<sup>37-41</sup> The control afforded by gas-phase experiments provides the ability to systematically manipulate reactivity-related factors such as particle size, charge, and stoichiometry. Fast-flow laserablation ion sources allow the production of both bare and reacted clusters,<sup>42</sup> enabling the characterization of reactants, products, and potentially intermediates or transition states of model catalytic reactions using gas-phase spectroscopic techniques.<sup>43,44</sup> These species have the added benefit of being computationally tractable, enabling experimentalists and theorists to develop a clear, molecular-scale understanding of catalytic reaction mechanisms which is difficult to obtain from bulk experiments alone.

The experimental spectroscopic characterization of bare  $(TiO_2)_n$  clusters constitutes a growing body of work, <sup>45–47</sup> including contributions from our laboratory.<sup>48,49</sup> Less work has been done to probe species formed from the reaction of small  $(TiO_2)_n$  clusters with a discrete number of water molecules,

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which can either adsorb molecularly or dissociatively as on the bulk surface. The hydration of cationic TiO<sup>+</sup> by up to 60 water molecules has been studied by mass spectrometry, though this measurement does not provide insight into the structure of the resultant clusters.<sup>50</sup> These solvated cations have been structurally characterized using infrared action spectroscopy by Zheng and co-workers,<sup>51</sup> who have also performed anion photoelectron spectroscopy (PES) on the anionic  $(TiO_2^-)(H_2O)_{0-7}$  clusters.<sup>52</sup> In both cases, their spectra indicated dissociative adsorption of water to form hydroxide species. Weichman and co-workers<sup>53</sup> have recently used infrared action spectroscopy to systematically characterize the anionic  $(TiO_2)_n^-(D_2O)_m$  clusters for n = 2-4 and m = 1-3, finding that the dissociative geometries are preferred for these clusters as well.

A number of groups have used theoretical treatmentsmost commonly density functional theory (DFT)-to assess the extent to which  $H_2O$  molecules dissociate on small  $(TiO_2)_n$ clusters.<sup>54–56</sup> The most comprehensive work in this area has been carried out by Dixon and co-workers,<sup>57,58</sup> who used a hybrid genetic algorithm to determine the lowest-energy structures for  $(TiO_2)_n(H_2O)_m$  (*n* = 1–4, *m* = 1–2*n*) clusters.<sup>59</sup> Geometry optimizations and single point calculations were carried out using both DFT and coupled cluster methods, yielding similar results for all model chemistries used. For the simplest stoichiometric  $TiO_2$ /water reaction,  $TiO_2 + H_2O$ , they found that the di-hydroxyl TiO(OH)2 structure, in which the water is split, is preferred over molecular adsorption  $(TiO_2 \cdot H_2O)$  by over 40 kcal mol<sup>-1</sup>. Of the two dissociatively adsorbed structures reported, the planar  $C_{2\nu}$  cis-hydroxyl isomer was found to be more stable than the  $C_s$  trans-OH isomer, though the energy difference was less than 3 kcal mol<sup>-1</sup>.

The only experimental work on this system comes from the aforementioned anion PES study by Zheng and coworkers,<sup>52</sup> who reported the photodetachment spectrum for TiO<sub>3</sub>H<sub>2</sub><sup>-</sup> formed by a laser ablation reactor source. This spectrum showed a single broad electronic band spanning ~1 eV in electron binding energy (eBE), reflecting extended unresolved vibrational progressions. From this spectrum, they estimated an electron affinity (EA) of  $1.15 \pm 0.8$  eV and a vertical detachment energy (VDE) of  $1.51 \pm 0.08$  eV. By comparison to their photoelectron spectrum of bare TiO<sub>2</sub><sup>-</sup> and DFT calculations, the anion geometry was assigned to the TiO(OH)<sub>2</sub><sup>-</sup> dissociative adduct. Other than the general assignment based on the position of the detachment feature, little information regarding the structure of the TiO<sub>3</sub>H<sub>2</sub><sup>-/0</sup> species can be gleaned from this work.

Slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI) is a high-resolution variation of traditional anion PES which provides vibrationally resolved detachment spectra reflecting the geometric and vibronic structure of the anion and neutral. Previously, we have used cryo-SEVI to characterize the unreacted  $TiO_2^-$  monomer;<sup>48</sup> here, we probe the  $TiO_3H_2^-$  species, corresponding to a single  $TiO_2^-$  reacted with one water molecule. These spectra represent a significant improvement in resolution compared to the work of Zheng and co-workers, showing an extensive vibrational structure with typical peak widths of 10 cm<sup>-1</sup> full-width at half-maximum (fwhm). With the assistance of DFT calculations, we assign the anion structure to the dissociative

di-hydroxide TiO(OH)<sub>2</sub><sup>-</sup> isomer identified as the lowestenergy neutral geometry by Dixon and co-workers. Several vibrational frequencies for the neutral TiO(OH)<sub>2</sub> species are extracted, as well as its EA. A comparison to the unreacted TiO<sub>2</sub><sup>-</sup> cryo-SEVI spectra elucidates the energetic effect of charge on the TiO<sub>2</sub><sup>-/0</sup> + H<sub>2</sub>O reaction, highlighting the utility of small metal oxide clusters as tools for understanding catalytic reactions.

# **II. EXPERIMENTAL METHODS**

The cryo-SEVI technique and apparatus have been previously described in detail.<sup>60–62</sup> For the current work, modifications to the previously described cryo-SEVI laser ablation ion source<sup>62</sup> were carried out to provide access to species formed by the reaction of gas phase clusters with reactant molecules of interest, introduced via a pulsed Series 9 General Valve. The design implemented is loosely based on the Smalley fast flow cluster reactor<sup>42</sup> and is similar to that used by Jarrold and coworkers.<sup>63</sup> As in previous experiments, the frequency-doubled output of a 20 Hz Nd: YAG laser (2-3 mJ/pulse) impinges on a rotating and translating titanium target, forming a plasma. A pulse of helium gas (150 psi backing pressure, pulse width  $60 \mu s$ ) from an Even-Lavie valve<sup>64</sup> entrains the plasma and the resultant mixture condenses and cools to form charged and neutral molecules and clusters in an 80 mm long, 2 mm diameter growth channel. These then pass through a 1 mm slit and into a second channel (90 mm long, 2 mm diameter), where a second pulsed valve introduces helium bubbled through room temperature H<sub>2</sub>O (15 psi backing pressure, pulse widths of  $\sim$ 160 µs). This second channel serves as a reactor channel in which the ablation products cool further, react with H<sub>2</sub>O, and then expand into vacuum.

Anions formed in the source are directed through a radiofrequency (rf) hexapole ion guide and rf quadrupole mass filter, which are used to select the relevant mass window from the distribution of species formed in the ablation channels. This ion packet is then confined in a rf octupole ion trap held at 5 K and filled with a buffer gas mixture of 20:80 H<sub>2</sub>:He. Collisions with the cold buffer gas result in effective vibrational, rotational, and electronic cooling of the ions, leading to typical internal temperatures around 10 K.<sup>62,65</sup>

The ions are trapped for ~40 ms, after which they are extracted into an orthogonal Wiley-McLaren time-of-flight mass spectrometer.<sup>66</sup> The mass-separated ions are focused into the interaction region of a velocity-map imaging (VMI) electrostatic lens assembly,<sup>67,68</sup> where the ions of interest are photodetached by a pulse of vertically polarized light. Here, the m/z = 98 peak was chosen, which should contain some contribution from <sup>50</sup>TiO<sub>3</sub><sup>-</sup> in addition to the target <sup>48</sup>TiO<sub>3</sub>H<sub>2</sub><sup>-</sup> species. However, given that the electron affinity of TiO<sub>3</sub> is quite high (4.2 eV)<sup>45</sup> relative to the detachment energies used in this work (<2 eV), this species does not contribute to the spectra.

The detachment laser configuration is based on a tunable dye laser pumped by the second harmonic of a 20 Hz Nd: YAG laser. For photon energies above ~1.3 eV (10 500 cm<sup>-1</sup>, 950 nm), the output of the dye laser is used without further modification. For photon energies below 1.3 eV, the output of

the dye laser is focused into a 63-cm long Raman cell containing 400 psi of H<sub>2</sub>. The Q<sub>1</sub>(1) line in the H<sub>2</sub> Raman spectrum is used to red-shift the dye light by 4155 cm<sup>-1</sup>,<sup>69</sup> producing tunable photon energies ranging from ~1.0 to 1.3 eV (8000-10 500 cm<sup>-1</sup>, 1200-950 nm). Residual dye light as well as anti-Stokes shifted light is separated from the Stokes-shifted light by a long-pass dichroic mirror (900 nm cutoff). The Ramanshifted light is very slightly depolarized,<sup>70</sup> and thus is passed through a linear polarizer to ensure vertical polarization in the interaction region.

Photoelectrons ejected in the interaction region of the VMI assembly are projected onto a 2D detector comprising two chevron-stacked microchannel plates coupled to a phosphor screen, which is photographed using a CCD camera.<sup>71</sup> Each photo is analyzed for individual electron events, the centroids of which are calculated and binned in a 2200  $\times$  2200 grid.<sup>72</sup> Slight deviations from circularity in the accumulated images are corrected using the circularization algorithm described by Gascooke and co-workers.<sup>73</sup> The electron velocity distribution is then reconstructed from the circularized images using the Maximum Entropy Velocity Legendre Reconstruction (MEVELER) algorithm.<sup>74</sup> 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<sup>-</sup> and O<sup>-</sup> at several photon energies.<sup>75,76</sup>

In addition to the eKE distributions, the MEVELER reconstruction of VMI images provides the photoelectron angular distribution (PAD) associated with each detachment transition, given by<sup>77</sup>

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

where  $\sigma_{tot}$  is the total detachment cross section,  $P_2(x)$  is the second-order Legendre polynomial,  $\theta$  is the angle of the outgoing photoelectron velocity vector with respect to the laser polarization axis, and  $\beta$  is the anisotropy parameter. The anisotropy parameter, which ranges from -1 (perpendicular detachment) to +2 (parallel detachment), reflects the angular momenta of the detached electrons and thus provides information regarding the electronic character of each transition.<sup>78</sup>

Due to the roughly constant resolving power,  $\Delta eKE/eKE$ , of the VMI spectrometer,<sup>67,68</sup> the best eKE resolution is obtained for slow electrons. Thus, a SEVI spectrum is acquired by first taking an overview spectrum at a relatively high photon energy, then tuning the detachment laser to energies slightly above features of interest. This results in a collection of narrow, high-resolution spectral windows that are then scaled to match overview intensities, which are less sensitive to the variation of photodetachment cross section with photon energy. The highresolution windows are spliced together to yield a complete photoelectron spectrum with sub-meV resolution. Spectra are plotted as a function of electron binding energy (eBE), given by eBE = hv - eKE.

# **III. COMPUTATIONAL METHODS**

Possible minimum-energy structures for both anionic and neutral  $TiO_2 + H_2O$  were explored using a variety of DFT-based model chemistries. The preliminary results suggested meaningful differences between model chemistries. Therefore, initial benchmarking calculations were carried out to compare six DFT-based model chemistries with the results of coupled-cluster singles and doubles (CCSD) calculations,<sup>79,80</sup> as summarized in Sec. S1 of the supplementary material. Based on comparisons of these CCSD results to DFT-predicted energetic ordering of candidate anion and neutral minimum energy structures as well as vertical and adiabatic detachment energies (ADEs) (Tables S1 and S2 in the supplementary material), the Becke-93 exchange and Yang-ParrLee correlation functionals (B3LYP) were employed with the Def2TZVP basis set,<sup>81–85</sup> and this model chemistry has been employed for the calculations described below.

Both doublet and quartet states were considered for anion candidates; singlet (closed-shell and open-shell) and triplet states were considered for the neutral candidates. For all identified structures, doublet anions are more stable than quartet species and the closed-shell singlet state was found to be more stable than the open-shell singlet or triplet state. Excited state calculations were carried out using the same model chemistry within the time-dependent DFT (TDDFT) formalism.<sup>86–88</sup> Analysis of these excited state calculations was facilitated by Martin's Natural Transition Orbital (NTO) model.<sup>89</sup>

All calculations were carried out using a local development version of the GAUSSIAN suite of electronic structure programs.<sup>90</sup> Converged Kohn-Sham determinants were tested for stability.<sup>91,92</sup> Molecular geometries were optimized using standard methods<sup>93</sup> and the reported potential energy minima were verified using analytical second-derivative calculations. Franck-Condon (FC) spectra were simulated using the implementation by Bloino, Barone, and co-workers.<sup>94,95</sup> Care was taken to determine appropriate scaling factors for the DFT force constants calculated for the lowest-energy neutral state (Table S3 of the supplementary material) such that simulated FC progressions aligned well with the experimental spectra. Further details of the FC simulations can be found in Sec. S2 of the supplementary material.

To describe the nature of the detached electron we have employed the Natural Ionization Orbital (NIO) model of Thompson, Harb, and Hratchian.<sup>96</sup> The NIO model provides a compact orbital representation of ionization processes by utilizing one-particle difference densities. Natural orbital analysis involving this difference density yields a simplified interpretation of electronic detachment processes. The NIO model has recently been shown to provide a convenient means to distinguish between one-electron transitions and those where the one-electron process is accompanied by excitation of a second electron into the virtual orbital space.<sup>97</sup> The current system is Koopmans-like, evidenced by the strong resemblance between the NIO and the canonical highest-occupied molecular orbital (HOMO) of the 1-1a anion (Fig. S1 of the supplementary material), and thus the detachment transitions considered here are one-electron transitions that can be equivalently described by considering the NIO or the anion HOMO. As such, the method of Liu and Ning<sup>98</sup> was applied to the HOMO of the lowestenergy anion to calculate the eKE-dependent PAD expected for the removal of an electron from this orbital; the results are shown as the solid lines in Fig. 2 and discussed further in Sec. VA.

#### IV. EXPERIMENTAL RESULTS

The cryo-SEVI spectrum for detachment from TiO<sub>3</sub>H<sub>2</sub>is shown in Fig. 1. In this figure, the blue trace corresponds to an overview scan taken with a relatively high detachment energy and the black traces are higher resolution SEVI scans taken with variable photon energies. The overview spectrum spans 10 000-13 500 cm<sup>-1</sup> in eBE and exhibits considerable vibrational structure, revealing increasing spectral congestion as the eBE increases. Due to this increased complexity, our analysis will be focused on the first  $\sim 2000 \text{ cm}^{-1}$  of structure. In this region, the high-resolution scans reveal a number of transitions (A1-11 and B1-11) with typical peak widths of  $\sim 10 \text{ cm}^{-1}$  fwhm, corresponding to detachment to different vibronic levels of the neutral TiO<sub>3</sub>H<sub>2</sub> species. The sharp onset of structure at peak A1 gives an EA of 1.2529(4) eV for TiO<sub>3</sub>H<sub>2</sub>. The remainder of the spectrum is dominated by a  $\sim 675 \text{ cm}^{-1}$  progression (A1-3-7-11), modulated by several weaker patterns. Peak positions, widths, and shifts from the origin are summarized in Table I.

The EA provided by cryo-SEVI is larger than the value of 1.15(8) eV reported by Zheng and co-workers.<sup>52</sup> This discrepancy is understandable given the lower resolution of their spectrum and the experimental conditions used to obtain it. In that work, individual transitions in the extended Franck-Condon progressions blend together to form a broad structureless feature, and the lack of a clear onset complicates the extraction of the EA. Additionally, the ions probed in the previous work were not cooled prior to detachment, and given the relatively high temperatures typical of ions produced by laser ablation,<sup>99</sup> the resultant spectra likely contain contributions from hot bands that can occur lower the apparent electron binding energy relative to the true EA. Hot bands are effectively eliminated in the cryo-SEVI experiment, where ions are cooled to ~10 K prior to detachment.<sup>65</sup>

Measurement of the PADs of features labeled in Fig. 1 (Fig. S2 of the supplementary material) reveals that all transitions fall into one of two groups with distinct angular distributions. These two groups are represented in Fig. 2, which plots the anisotropy parameter ( $\beta$ ) versus eKE for peaks A1-3 and B1-3. Features A1-3 show positive values of  $\beta$ , whereas features B1-3 show isotropic ( $\beta \sim 0$ ) angular distributions. The remainder of features in Fig. 1 shows PADs that are qualitatively similar to one of these two groups, and are labeled

TABLE I. Peak positions, shifts from the vibrational origin, qualitative anisotropy parameters (+ or 0), and vibrational assignments for features in the cryo-SEVI spectrum of TiO<sub>3</sub>H<sub>2</sub><sup>-</sup>. Uncertainties in peak positions correspond to one standard deviation ( $\sigma$ ) obtained from a Gaussian fit to the highest-resolution scan of the experimental peak, which is related to the fwhm by fwhm =  $2\sqrt{2\ln 2\sigma}$ .

Peak	eBE (cm <sup>-1</sup> )	Shift (cm <sup>-1</sup> )	β	Assn.
A1	10 106(3)	0	+	00
B1	10165(3)	60	0	8 <sup>1</sup> <sub>0</sub>
A2	10519(2)	413	+	$4^{1}_{0}$
B2	10 576(2)	471	0	$4^1_0 8^1_0$
A3	10784(3)	678	+	$3^{1}_{0}$
В3	10846(3)	741	0	$3^1_0 8^1_0$
A4	10 926(6)	820	+	$3_0^1 8_0^2$
B4	10987(7)	881	0	$3_0^1 8_0^3$
A5	11 121(5)	1016	+	$2^{1}_{0}$
A6	11 199(4)	1093	+	$3^1_0 4^1_0$
B6	11 258(4)	1152	0	$3_0^1 4_0^1 8_0^1$
A7	11 459(3)	1354	+	$3_0^2$
B7	11 524(3)	1418	0	$3_0^2 8_0^1$
A8	11607(13)	1501	+	$3_0^2 8_0^2$
B8	11673(12)	1568	0	$3_0^2 8_0^3$
A9	11798(5)	1692	+	$2^1_0 3^1_0$
A10	11 874(6)	1769	+	$3_0^2 4_0^1$
B10	11936(4)	1831	0	$3_0^2 4_0^1 8_0^1$
A11	12 133(4)	2027	+	$3_0^3$
B11	12 200(6)	2095	0	$3_0^3 8_0^1$

accordingly, where peaks labeled A correspond to parallel  $(\beta > 0)$  detachment transitions and peaks labeled B have isotropic  $(\beta \sim 0)$  PADs. These anisotropy parameters are summarized qualitatively in Table I. Each B-series transition lies  $\sim 60 \text{ cm}^{-1}$  above a peak in the A1-11 series, and has been numbered accordingly.

These two groups also show distinctly different dependencies of the photodetachment cross section on eKE. Far from threshold, the A1-11 series dominates the spectrum, as can be seen in the overview spectrum in Fig. 1. As the photon energy is lowered, transitions in the B1-11 series become more



FIG. 1. Cryo-SEVI spectrum of  $\text{TiO}_3\text{H}_2^-$ . The blue trace is an overview spectrum taken with a photon energy of 13 721 cm<sup>-1</sup>, and the black traces are high-resolution scans taken at variable photon energies. Black traces are scaled to match relative peak intensities observed in the overview as much as possible. The red stick spectrum shows the Franck-Condon simulation for detachment from the **1-1a**  $C_{2v}$  cis-OH TiO(OH)<sub>2</sub><sup>-</sup> geometry using neutral frequencies that have been scaled as described in Table S3 of the supplementary material.



FIG. 2. Anisotropy parameters of peaks A1-3 and B1-3 extracted from VMI images obtained at multiple photon energies, showing the distinctly different PADs for the two groups of features. The solid line shows the calculated anisotropy parameter expected for detachment from the **1-1a** anion HOMO found by DFT.<sup>98</sup>



FIG. 3. Detachment spectra of  $\text{TiO}_3\text{H}_2^-$  at several photon energies illustrating the greater extent of signal attenuation for peak A1 versus peak B1 as eKE decreases. The intensity of each scan has been normalized to the intensity of peak B1. Photon energies used are 10 568 (blue), 10 297 (red), and 10 215 cm<sup>-1</sup> (black).

apparent, resulting from the relative attenuation of the A1-11 peaks. This trend is illustrated in Fig. 3, where peaks A1 and B1 are shown for several photon energies and the intensities are normalized to the peak intensity of B1. The relative scaling of detachment cross sections for low-eKE detachment is given by the Wigner threshold law,<sup>100</sup>

$$\sigma \propto (\mathrm{eKE})^{l+1/2},\tag{2}$$

where  $\sigma$  is the detachment cross section and l is the angular momentum of the detached electron. According to this law, a sharper decrease in detachment signal as the photon energy is lowered reflects higher l detachment channels; it can therefore be inferred that transitions A1-11 correspond to higher ldetachment than transitions B1-11.

#### V. DISCUSSION

# A. Structural assignment of TiO<sub>3</sub>H<sub>2</sub><sup>-</sup>

Figure 4 shows optimized minimum-energy structures located on the anionic and neutral  $TiO_3H_2$  potential energy surfaces, as well as zero-point corrected energies. Cartesian coordinates for these structures are provided in Secs. S3 and S4 of the supplementary material. In agreement with previous

work by Dixon and co-workers,<sup>59</sup> the  $C_{2v}$  dissociative structure (1-1a') is found to be the lowest-energy neutral geometry; likewise, the 1-1a geometry is the lowest-energy anion isomer. Two additional minimum-energy structures, 1-1b and 1-1e, were found on the anion potential energy surface to lie 0.08 and 0.19 eV above **1-1a**, respectively, and differ from this isomer by rotation of the hydroxide groups. A local minimum corresponding to the *trans*-OH 1-1b' geometry was discovered at an energy of 0.11 eV above the neutral 1-1a' structure, in reasonable agreement with the relative energy reported by Dixon. No neutral minimum corresponding to the 1-1e isomer was identified. The lowest-energy molecularly adsorbed TiO<sub>3</sub>H<sub>2</sub> adduct reported by Dixon was also identified as a local minimum for both anion (1-1c) and neutral (1-1c'), though these structures lie 2.34 and 3.13 eV above the anion and neutral global minima, respectively.

Given the relative energies of the anion geometries shown in Fig. 4, the most likely structures contributing to the cryo-SEVI spectrum of TiO<sub>3</sub>H<sub>2</sub><sup>-</sup> correspond to the dissociative geometries 1-1a and 1-1b. The assignment of a dissociatively adsorbed anion geometry is consistent with the assessment of Zheng and co-workers.<sup>52</sup> Predicted adiabatic detachment energies (ADEs) for 1-1a and 1-1b are 1.23 and 1.26 eV, respectively, both in good agreement with the experimental electron affinity (1.25 eV). In both cases, NIO analysis clearly indicates that the detached electron resides in the anion HOMO, which strongly resembles the Ti  $d_{z^2}$  orbital (see Fig. 5 and Fig. S3 of the supplementary material). Analysis of the NIO for either 1-1a or 1-1b gives an orbital angular momentum of L = 2, such that detachment from either of these orbitals would be expected to primarily yield outgoing p- (l = 1) and f-wave (l = 3) electrons. This high-*l* detachment is consistent with the observed attenuation of the signal near threshold for peaks A1-11.

Additionally, the eKE-dependence of the anisotropy parameter calculated<sup>98</sup> for detachment from the **1-1a** HOMO (Fig. 2, solid lines) is in good agreement with the measured  $\beta$  values for peaks A1-11, showing positive values in the eKE region of interest. Given the similarity between the **1-1a** and **1-1b** NIOs, detachment from the **1-1b** isomer is expected to have a similar PAD. The agreement between experiment and theory further supports the conclusion that the global minimum of the TiO<sub>3</sub>H<sub>2</sub><sup>-</sup> anion takes the dissociative TiO(OH)<sub>2</sub><sup>-</sup> dihydroxide geometry and that detachment from one of these isomers to the ground state of the corresponding neutral accounts for the most intense structure (A1-11).

To determine definitively which of these species is responsible for the experimentally observed detachment transitions, we consider the Franck-Condon profiles for detachment from both isomers, as the FC profile is highly sensitive to the anion and neutral geometries. Figures S4 and S5 of the supplementary material show the experimental overview spectrum overlaid with FC simulations for detachment from the ground electronic state of the **1-1a** and **1-1b** anion, respectively, to the closed-shell singlet state of the corresponding neutral. To provide a better comparison to experiments, Figs. S6 and S7 of the supplementary material show FC profiles calculated using neutral vibrational frequencies that have been scaled as described in Table S3 of the supplementary material. Of these two 222810-6 DeVine et al.



FIG. 4. Optimized geometries of anionic and neutral  $TiO_3H_2$  found with B3LYP/Def2TZVP. Energies are provided relative to the **1-1a** geometry of the anion and include zero-point corrections. Geometric parameters are also provided.

isomeric candidates, the FC profile for detachment from the  $\tilde{X}^2A_1$  state of the **1-1a** anion (Figs. S4 and S6 of the supplementary material) provides better agreement with experiment than detachment from the  $\tilde{X}^2A'$  **1-1b** anion (Figs. S5 and S7 of the supplementary material). The calculation in Fig. S6 of the supplementary material using scaled frequencies is shown in red in Fig. 1 and reproduces the dominant vibrational structure observed in the experimental spectrum. In particular, the first several intense features (A1-3) are reproduced in the FC simulation for **1-1a**, whereas the **1-1b** simulation shows extra structure between A1 and A3. Thus, we assign the **1-1a** *cis*-OH geometry as the lowest-energy isomer of TiO<sub>3</sub>H<sub>2</sub><sup>-</sup>, and the observed spectral features reflect the vibronic structure of the corresponding **1-1a'** neutral.

#### **B.** Vibrational assignments

The agreement between the simulated and experimental spectra in Fig. 1 enables straightforward assignment of the major structure (A1-11) as  $\tilde{X}^1A_1 \leftarrow \tilde{X}^2A_1$  detachment transitions terminating in totally symmetric vibrational levels of the neutral ground state (Table I). The less intense B1-11 series of peaks are not fully described by this FC simulation, and the previously described PADs indicate that these transitions do not have the same electronic character as A1-11. As such, we will first address the vibrational assignments of A1-11.



FIG. 5. NIO describing the electron detachment from the **1-1a** anion to the ground electronic state of the corresponding **1-1a'** neutral species.

The dominant progression (A1-3-7-11) is assigned to the  $v_3$  vibrational mode, which corresponds to a symmetric Ti—OH stretching motion (Fig. S8 of the supplementary material). The shift of peak A3 from the vibrational origin (A1) gives a frequency of 678(5) cm<sup>-1</sup> for this mode. There is also significant participation of the  $v_4$  totally symmetric OH wagging mode in the spectrum (A2, A6, A10), as well as some activity in the  $v_2$  terminal Ti=O stretch (A5, A9). The shifts of peaks A5 and A2 give neutral vibrational frequencies of 1016(8) and 413(3) cm<sup>-1</sup> for  $v_2$  and  $v_4$ , respectively. Table II summarizes the energetic quantities for neutral TiO(OH)<sub>2</sub> extracted from experiment and compares them to the **1-1a'** B3LYP/Def2TZVP results, showing reasonably good agreement for these totally symmetric modes.

The Franck-Condon activity of different normal modes can be rationalized by considering the geometrical changes that occur upon photodetachment, which are summarized for the B3LYP/Def2TZVP **1-1a**  $\tilde{X}^2A_1$  anion and **1-1a'**  $\tilde{X}^1A_1$  neutral equilibrium geometries in Table S4 of the supplementary material. The most significant change is a 13.6° increase in the H—O—Ti bond angle, which results in the FC activity of the  $v_4$ OH-wagging mode. The involvement of the titanium-oxygen stretching modes  $v_2$  and  $v_3$  is a reflection of the change in bond lengths upon photodetachment for both the terminal Ti=O bond as well as the hydroxide Ti—O bonds. The hydroxide and terminal Ti—O bonds of the B3LYP geometries decrease by 0.08 and 0.05 Å, respectively, corresponding to modest 3%-4% decreases in these bond lengths. These constitute the

TABLE II. Electronic and vibrational energies for neutral **1-1a'**  $TiO(OH)_2$  extracted from the  $TiO_3H_2^-$  cryo-SEVI spectrum, and compared to the (unscaled) results obtained from B3LYP/Def2TZVP calculations.

	Cryo-SEVI	B3LYP/Def2TZVP
EA (eV)	1.2529(4)	1.2341
$v_2 ({\rm cm}^{-1})$	1016(8)	1062
$v_3 ({\rm cm}^{-1})$	678(5)	683
$v_4 ({\rm cm}^{-1})$	413(3)	485
$v_8 ({\rm cm}^{-1})$	60(4)	16

second- and third-largest fractional changes upon detachment for the five geometrical parameters summarized in Table S4 of the supplementary material.

While the above considerations fully assign peaks A1-11, the differing PADs and threshold behavior of peaks B1-11 indicate that these transitions have different electronic character, ruling out assignment to Franck-Condon allowed transitions within the  $\tilde{X}^1 A_1 \leftarrow \tilde{X}^2 A_1$  electronic band including vibrational hot bands. These transitions are also unlikely to correspond to detachment from an excited anion state, as a TDDFT calculation for the anion (Table S5 of the supplementary material) does not reveal an excited state with sufficiently low excitation energy to be populated in the cold trap, where ions typically have temperatures on the order of 10 K. It is possible that peaks B1-11 arise from detachment to a separate electronic state of neutral TiO(OH)<sub>2</sub>, and that the two groups of features correspond to overlapping electronic bands with the A1-B1 spacing providing the electronic term energy. However, this would require a neutral state with a term energy of around 60 cm<sup>-1</sup>, and the present theoretical results do not provide evidence for such a state, with the lowest-energy neutral excited state of 1-1a' lying 3.86 eV above the closed-shell singlet (Table S5 of the supplementary material).

Another possible assignment for peaks B1-11 is detachment from a different TiO<sub>3</sub>H<sub>2</sub><sup>-</sup> geometry. In the current theoretical framework, the 1-1b trans-OH TiO(OH)<sub>2</sub><sup>-</sup> dissociative adduct is expected to be only 0.08 eV higher than the cis-OH (1-1a) isomer. Given this low relative energy as well as its structural similarity to the global minimum, this geometry could interconvert with the slightly more stable **1-1a** geometry in the ion trap, resulting in contributions from multiple isomers in the cryo-SEVI spectrum. However, the barrier for conversion of the 1-1a isomer to the 1-1b geometry is estimated to be  $\sim 1300 \text{ cm}^{-1}$  from constrained optimization and single point calculations (Fig. S9 of the supplementary material), indicating that such interconversion is highly unlikely in the cold environment of the ion trap. Additionally, as discussed above, the NIOs for the 1-1a and 1-1b isomers are quite similar (Fig. 5 and Fig. S3 of the supplementary material), with both orbitals dominated by Ti  $d_{z^2}$  character. Thus, if detachment features from the 1-1b geometry were observed, the transitions would not have PADs that deviate so significantly from the cis-OH detachment transitions, ruling out assignment of peaks B1-11 as detachment from the 1-1b anion. A similar argument can be made to rule out detachment from the **1-1e** isomer, which also differs from 1-1a only by rotation of the hydroxyl groups.

Given the above considerations, and the observation that each of the B1-11 features lies ~60 cm<sup>-1</sup> above a transition in the A1-11 series, we conclude that these features correspond to detachment transitions terminating in  $\tilde{X}^1A_1$ vibrational levels with odd quanta of excitation along a lowfrequency non-totally symmetric mode. These FC-forbidden transitions obtain their oscillator strength and PADs through Herzberg-Teller (HT) coupling to an excited neutral electronic state.<sup>101</sup> The most likely vibrational assignment for peaks B1-11 involves the  $b_1$ -symmetric  $v_8$  mode, which corresponds to the umbrella-like motion of the Ti atom through the plane of the three oxygen atoms (Fig. S8 of the supplementary material) and has the lowest calculated frequency (Table S3 of the supplementary material) for the **1-1a'** neutral. Each B*i* transition in the B1-11 series is thus assigned as terminating in the state corresponding to the A*i* transition, plus a single quantum of excitation along  $v_8$ . With this assignment, the position of peak B1 relative to A1 gives a vibrational frequency of 60(4) cm<sup>-1</sup> for the  $v_8$  umbrella mode of neutral TiO(OH)<sub>2</sub>.

We now consider the symmetry requirements for the excited electronic state which gives rise to transitions B1-11 through Herzberg-Teller coupling. Consider a vibronic state  $|a\rangle$  whose electronic and vibrational symmetries are  $\Gamma^a_{elec}$  and  $\Gamma^a_{vib}$ , respectively. This state can undergo HT-coupling with another vibronic state,  $|b\rangle$ , with symmetries  $\Gamma^b_{elec}$  and  $\Gamma^b_{vib}$ , provided

$$\Gamma^{a}_{elec} \otimes \Gamma^{a}_{vib} \otimes \Gamma^{b}_{elec} \otimes \Gamma^{b}_{vib} \supset \Gamma_{TS}, \tag{3}$$

where  $\Gamma_{TS}$  is the totally symmetric representation within the relevant molecular point group. If state *b* is FC-allowed for detachment from the anion in question (i.e.,  $\langle b | \Psi_{anion} \rangle \neq 0$ ), detachment to state *a* will reflect the *b*-state electronic character, which will be observable in the PAD and threshold behavior.

In the current case, the observed HT-coupled levels correspond to states with odd quanta of excitation along the  $b_1$ -symmetric  $v_8 \mod (\Gamma_{vib}^a = b_1)$  within the vibrational manifold of the ground neutral electronic state ( $\Gamma_{elec}^a = A_1$ ). Within the  $C_{2\nu}$  point group, these levels are Franck-Condon forbidden, and so can only be observed if they mix with some vibronic level b that is not FC-forbidden, i.e.,  $\Gamma_{vib}^b = a_1$ . Thus, the observed features must arise from HT-coupling with a  $B_1$ symmetric electronic excited state. The lowest such singlet state identified from TDDFT (Table S5 of the supplementary material) is the relatively high-lying  $\tilde{C}^1 B_1$  excited state, residing 4.45 eV above neutral  $\tilde{X}^1A_1$  **1-1a'**. Using the NTO model, we determined that this state would involve detachment from an orbital with angular momentum L = 1, resulting in outgoing s- (l = 0) and d-wave (l = 2) electrons, in contrast to the p- and f-wave detachment expected from the 1-1a NIO. Thus, the assignment of peaks B1-11 as arising from Herzberg-Teller coupling to this  ${}^{1}B_{1}$  state is consistent with the observed relative attenuation of A1-11 versus B1-11 as photon energy is lowered.

### C. Charge effects on the $TiO_2 + H_2O$ reaction

The cryo-SEVI spectrum of unreacted TiO<sub>2</sub><sup>-</sup> has been previously reported, giving an electron affinity of 1.5892(5) eV for the singlet ground state of TiO<sub>2</sub>.<sup>48</sup> The electron affinity of the TiO(OH)<sub>2</sub> dissociative adduct is lower by roughly 0.3 eV, and this difference provides insight into the energetic effects of charge on the dissociation of H<sub>2</sub>O by TiO<sub>2</sub>. The lower electron affinity for the reacted species implies that the neutral TiO<sub>2</sub> + H<sub>2</sub>O  $\rightarrow$  TiO(OH)<sub>2</sub> reaction is more exothermic than the anionic counterpart—that is, reaction with water to form the dissociative TiO(OH)<sub>2</sub> adduct stabilizes neutral TiO<sub>2</sub> more than it does the anion. As a consequence, it can be inferred that neutral TiO<sub>2</sub>, where the titanium center has a +4 oxidation state, is more reactive towards water than anionic TiO<sub>2</sub><sup>-</sup> where the Ti oxidation state is +3. The energies shown in Fig. 4 indicate that the molecularly adsorbed 1-1c' geometry has an even lower EA (0.79 eV) than the dissociative structures. Given that all the geometries in Fig. 4 involve binding interactions between the water oxygen and Ti, this charge effect likely derives from donation of electron density from the incoming water molecule to the metal center, which in turn is favored by a higher titanium oxidation state.

The enhanced reactivity towards water of neutral  $TiO_2$  echoes the electrochemical mechanism of water splitting in photoelectrochemical cells (PECs) where titania is used as a photoanode.<sup>14</sup> In these systems, the generally understood mechanism is initiated by photoexcitation of titania, resulting in the formation of an electron-hole pair. The electron is then transferred to the cathode, typically a metal, leaving behind a hole in the valence band of TiO<sub>2</sub>. These holes participate in the oxidation half-reaction,

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-,$$
 (4)

while the electrons at the cathode participate in the reduction half-reaction,

$$2\mathrm{H}^{+} + 2e^{-} \to \mathrm{H}_{2}.$$
 (5)

Within this mechanistic picture, the photosensitization of water by  $TiO_2$  is a consequence of the ability of  $TiO_2$  to donate a hole (or, equivalently, accept an electron). Direct parallels between the chemistry occurring in such PECs and the gas-phase  $TiO_2^{-/0}$  reaction considered here are difficult to make, due to the fundamental differences in the electronic structures for these two systems and the increased complexity associated with the condensed phase. However, it is interesting to note that the reactivity of  $TiO_2$  with water in the gas phase reflects, to some extent, the bulk electrochemical behavior—namely, the energetics of the  $TiO_2$ /water reaction are directly related to the oxidation state of the Ti center, with a more positively charged metal atom resulting in a more energetically favorable interaction with water.

#### **VI. CONCLUSION**

Vibrationally-resolved photoelectron spectra of the TiO<sub>3</sub>H<sub>2</sub><sup>-</sup> anion are obtained using slow electron velocitymap imaging of cryogenically cooled anions, yielding spectra that reflect the vibronic structure of neutral TiO<sub>3</sub>H<sub>2</sub>. These results provide a significant improvement in resolution over prior work on this system, clearly resolving the onset of the structure at the adiabatic detachment energy. A Franck-Condon simulation for detachment from the  $C_{2\nu}$ 1-1a TiO(OH)2<sup>-</sup> cis-hydroxide geometry captures the dominant vibrational structure observed experimentally, enabling the assignment of this geometry as the lowest-energy anion isomer in agreement with density functional theory calculations. In addition to transitions reproduced in the FC simulations, a series of features resulting from Herzberg-Teller coupling to an excited neutral electronic state is identified in the cryo-SEVI spectrum, evidenced by noticeable differences in the angular and energy dependence of the photodetachment cross sections.

The comparison of the current spectral results to the previously reported cryo-SEVI spectrum of unreacted  $\text{TiO}_2^-$  provides insight into the reactivity of  $\text{TiO}_2^{-/0}$  towards water.

The lowered electron affinity of  $TiO_3H_2$  relative to  $TiO_2$  indicates that neutral  $TiO_2$  is stabilized to a greater extent than anionic  $TiO_2^-$  by reaction with water, suggesting that the reaction of  $TiO_2$  with water is impeded by excess negative charges. This conclusion is consistent with the existing electrochemical understanding of photocatalytic water splitting by  $TiO_2$  in photoelectrochemical cells, where the sensitization of water arises from the ability of  $TiO_2$  to accept electron density. This work highlights the relevance of gas-phase studies of metal oxide cluster reactions to bulk catalytic reactions, as well as the utility of cryo-SEVI as a structural probe for such systems.

# SUPPLEMENTARY MATERIAL

See supplementary material for details regarding electronic structure and Franck-Condon calculations as well as Figs. S1–S9 and Tables S1–S5.

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