

Hydrogen-Bond Network Drives Water Splitting by Neutral Tantalum Center

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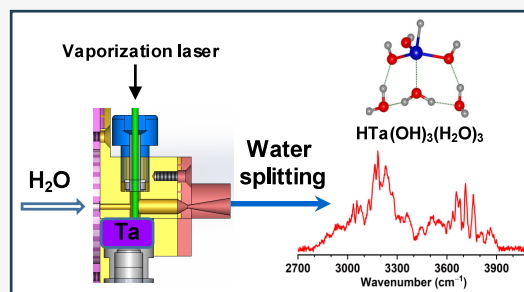


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ABSTRACT: Elucidating the water splitting by neutral metals is crucial for understanding the structure–reactivity relationship of catalysts. However, experimental characterization of such neutral metal–water systems remains extremely challenging due to the difficulty in mass selection. Herein, the reactions of neutral tantalum with water were studied by size-specific infrared–vacuum ultraviolet spectroscopy with the combination of quantum chemical calculations and ab initio molecular dynamics simulations. The agreement between experimental and theoretical results identifies the key products of stepwise solvated hydrides $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1–3$). The $n = 1$ monohydrate is stabilized by a cyclic double hydrogen bond motif between the $\text{HTa}(\text{OH})_3$ core and the water molecule, while subsequent hydration ($n = 2$ and 3) progressively extends this hydrogen bond network to form the first solvation shell. Significantly, the first water molecule in $\text{TaO}(\text{H}_2\text{O})_n$ inhibits the water dissociation reaction on TaO, whereas the second water molecule in $\text{TaO}(\text{H}_2\text{O})_n$ is able to trigger the water splitting facilitated by a six-membered hydrogen bond network. This work provides the direct spectral evidence of intrinsic structure and solvation effect of hydrolysis products and offers a molecular-level prelude to the macroscopic mechanism of single-atom catalysts for water splitting.



The activation and decomposition of water molecules by transition metals are core chemical processes in heterogeneous catalysis, photocatalytic water-splitting, and material corrosion science.^{1,2} For instance, tantalum and its oxides have attracted significant attention due to their excellent thermal stability, corrosion resistance, and promising electrocatalytic activity for the hydrogen evolution reaction in acidic media.^{3,4} Understanding the adsorption, dissociation, and hydrolysis of water on tantalum surfaces at the molecular level is fundamental for tailoring their catalytic performance.¹ However, it is very challenging to explore how local hydrogen bonding topologies regulate reactivity in heterogeneous catalysis^{5,6} and to capture the dynamic rearrangement of active sites in single-atom catalysts (SACs).^{7,8} To overcome the complexity of condensed-phase surfaces, gas-phase cluster chemistry provides an ideal research strategy.^{9,10} This approach enables precise probing of how metal centers induce or catalyze elementary reactions (i.e., proton transfer and hydrolysis) in a well-defined environment free from bulk or matrix interference.¹¹

Over the past two decades, infrared photodissociation (IRPD) spectroscopy has greatly advanced our understanding of gas-phase ionic metal–water reactions. The reactions of metal cations (e.g., TiO^+ ,¹² ScO^+ ,¹³ and their congeners VO^+ / NbO^+ ,¹⁴ etc.) with water have been systematically explored, revealing the transformations from physically adsorbed $\text{MO}^+(\text{H}_2\text{O})$ to chemically inserted $\text{M}(\text{OH})_2^+$ isomers and

proposing that the “water-assisted” mechanism can significantly reduce this energy barrier.¹¹ IRPD spectroscopic studies of the $\text{HAIOH}^+(\text{H}_2\text{O})_n$ system showed that hydrogen bonding toward the hydride starts at $n = 12$, indicative of the onset of hydrogen evolution.^{15,16} For the tantalum systems, recent IRPD studies of $\text{TaO}_2^+(\text{H}_2\text{O})_n$ cations have also demonstrated how microsolvation drives their hydrolysis to form the $\text{Ta}(\text{OH})_4^+$ core.^{17,18} Gas-phase kinetic studies indicated that small tantalum cluster cations could efficiently activate the O–H bonds of alcohols, leading to dehydrogenation and underscoring the intrinsic capability of tantalum centers to cleave hydroxyl bonds.¹⁹ The investigations of the reactions of water with doubly charged cations (e.g., Ta^{2+} and TaO^{2+}) revealed water-mediated proton transfer and sequential hydrolysis,²⁰ highlighting the critical role of charge state in modulating the reaction pathways.

Conventionally, spectroscopic studies of neutral metal–water reactions mainly rely on matrix-isolation infrared spectroscopy.^{21–24} For example, Zhou et al. captured the

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complex of Ta/Nb oxide and water in low-temperature inert gas and observed that light can induce its isomerization to $\text{HMO}(\text{OH})$ or $\text{MO}(\text{OH})_2$.²⁵ While matrix-isolation is a powerful tool for stabilizing and characterizing these complexes, the matrix effect causes the vibration frequency to shift as compared with the gas phase, and the low-temperature environment might limit the direct exploration of thermodynamically relevant conformations.^{26,27} To obtain complementary gas-phase information, techniques such as anion photoelectron spectroscopy (PES) and high-resolution slow photoelectron velocity-map imaging (cryo-SEVI) of cryogenically cooled anions have been fruitfully applied to related systems.^{28–31} For instance, these photodetachment methods have yielded valuable structural and energetic information on the neutral dissociative adducts of titanium, zirconium, and vanadium oxides.^{28–30} Although there have been many experimental and theoretical studies on the reactions of tantalum with water,^{11,17,18,22,25,32,33} the understanding of how the neutral tantalum atom activates the water molecule remains elusive, particularly due to the lack of direct gas-phase spectroscopic characterization of neutral products.

In this work, the reactions of the neutral Ta center with water were studied by using the size-specific infrared-vacuum ultraviolet (IR-VUV) spectroscopy. Neutral products of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1–3$) were observed and characterized by the combination of IR-VUV spectra with quantum chemical calculations and ab initio molecular dynamics (AIMD) simulations. Experimental and theoretical results reveal that the formation mechanism of the $\text{HTa}(\text{OH})_3$ core is both thermodynamically exothermic and kinetically facile by lowering the hydrolysis energy barrier through a six-membered hydrogen bond network assisted by a second water molecule.

The IR spectra of neutral $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1–3$) complexes were measured by using the IR-VUV depletion scheme (experimental details are given in the Supporting Information (SI)).^{34–36} Briefly, neutral $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ complexes were prepared by laser ablation of the tantalum target reacting with a $\text{H}_2\text{O}/\text{He}$ mixture, followed by pulsed supersonic expansion. The neutral clusters were excited by a tunable IR laser generated from an optical parametric oscillator/amplifier system (LaserVision), for which the IR pulse energy curve is shown in Figure S1. Photoionization was achieved by using a 193 nm laser pulse, introduced 150 ns after the IR laser pulse. The calculated vertical ionization potentials (VIPs) for the $n = 1–3$ clusters (Table S1) are slightly below 6.42 eV, indicative of a single-photon nonresonant ionization.

The VUV-ionized mass spectra for the IR spectral measurement of each individual cluster $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ are shown in Figure S2a–c, respectively. The size-specific IR spectra of neutral $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ were acquired via the depletion efficiency of VUV-ionized mass signal intensity of $[\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n]^+$ without and with IR laser (IR laser OFF minus IR laser ON) by scanning the wavelength of the IR laser. The experimental IR spectra of neutral $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1–3$) are in Figure 1E₁–E₃. The positions of the observed vibrational bands are summarized in Tables 1, S2, and S3, respectively. The experimental spectrum of $n = 1–3$ exhibits 7 (a–g), 9 (a–i), and 11 (a–k) characteristic bands, respectively. It can be seen that the experimental IR spectra of each individual cluster $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ are all different from each other (Figure 1E₁–E₃), indicating that the IR-VUV measurement of these IR spectra is free from spectral contamination. As shown in Figure S3, IR spectra extracted

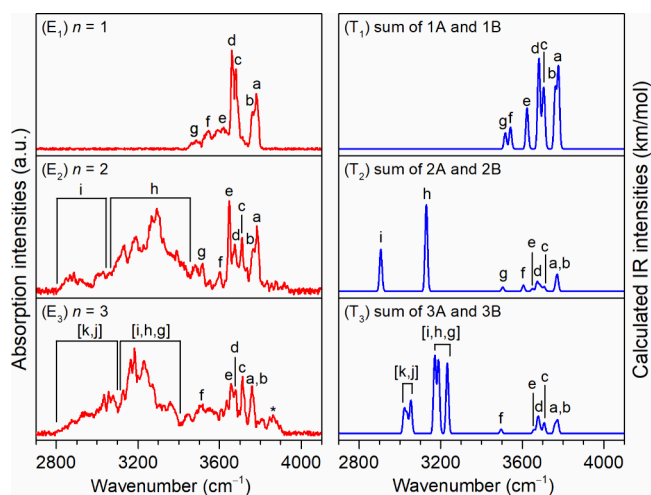


Figure 1. (E₁–E₃) Experimental IR spectra of neutral $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1–3$). (T₁–T₃) Theoretical IR spectra of a 1 ($n\text{A}$):1 ($n\text{B}$) mixture of isomers of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1–3$) calculated at the PBE0-D3(BJ)/def2-TZVP level of theory, with the harmonic vibrational frequencies scaled by a factor of 0.948.

from the $n = 1$ mass channel under the IR spectral measurement conditions for the $n = 1, 2$, and 3 clusters (Figure S2a–c) show essentially same spectral features and no obvious bands in the 2800–3300 cm^{-1} region that appear in the IR spectra of the $n = 2$ and 3 clusters (Figure 1E₂–E₃), indicating that there is no spectral contribution from larger clusters.

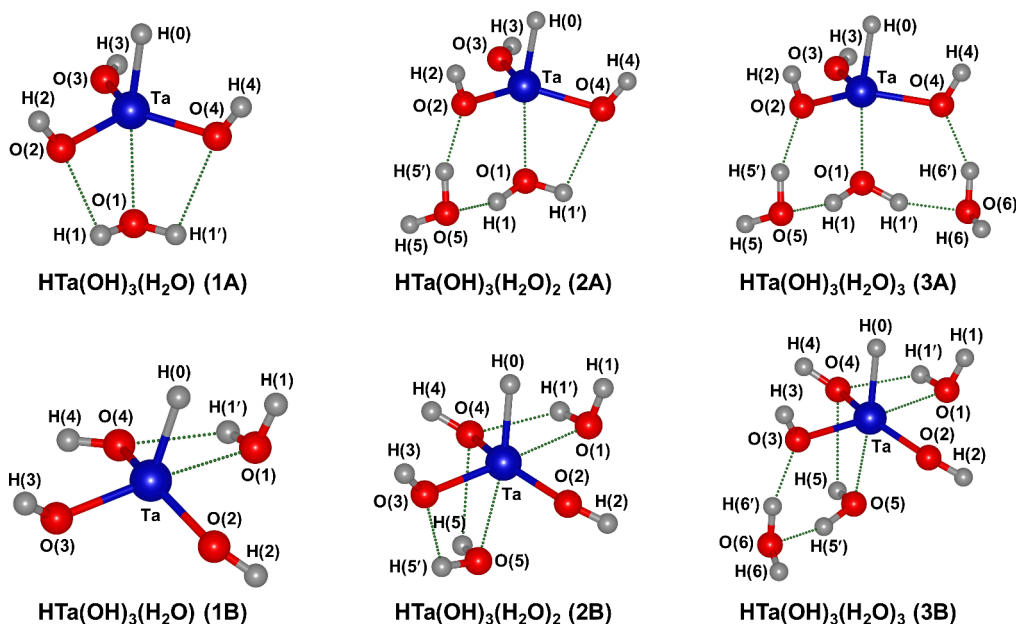
To interpret the experimental bands and identify the geometric structures of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1–3$), quantum chemical calculations were performed at the PBE0-D3(BJ)/def2-TZVP level, with relative energies refined by CCSD(T)/def2-TZVPP single-point calculations (see SI for theoretical details). The identified structures are shown in Figure 2, with their theoretical mixing spectra in Figure 1T₁–T₃. Detailed comparison of simulated IR spectra of the isomers with the experimental IR spectra is given in Figures S4–S6, respectively. The calculated frequencies for the $n = 1–3$ clusters are listed in Tables 1, S2, and S3, respectively.

As shown in Figure 2, the two lowest-energy isomers of each cluster adopt the $\text{HTa}(\text{OH})_3$ solvated structures with the doublet ground state (²A). For $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})$, isomers 1A and 1B are hydrated adducts in which the water molecule is terminally coordinated to the tantalum atom. In 1A, the water molecule forms two hydrogen bonds with the oxygen atoms of the Ta–OH groups, whereas 1B forms only one such hydrogen bond. They are virtually isoenergetic ($\Delta E = 0.1$ kcal/mol at the CCSD(T)/def2-TZVPP level). The barrier of the 1B → 1A isomerization is 10.6 kcal/mol at the CCSD(T)/def2-TZVPP level (*vide infra*), which might be sufficiently large so that the interconversion between isomers 1A and 1B does not readily occur in the cold molecular beam (estimated cluster temperature: 100–200 K). As shown in Figure S4, isomers 1C and 1D lie 15.4 and 56.2 kcal/mol above 1A at the CCSD(T)/def2-TZVPP level, respectively. The predicted IR spectra features of 1C in the 2800–3300 cm^{-1} range are not observed experimentally, implying that its contribution is negligible. Since isomer 1D cannot reproduce experimental bands c and d and lies too high in energy, it is excluded. The seven OH stretching vibration peaks in the experimental spectrum of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})$ cannot be fully explained by

Table 1. Comparison of the Experimental Band Positions (cm^{-1}) of Neutral $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})$ Complex to the Calculated Values of the Most Stable Structures (Isomers 1A and 1B) Obtained at the PBE0-D3(BJ)/def2-TZVP Level of Theory^a

Species	Isomer	Label	Exptl	Calcd	Mode
$\text{HTa}(\text{OH})_3(\text{H}_2\text{O})$	1A	a	3781	3778(238)	Stretching mode of the O(3)H(3) group
		d	3660	3680(77)	Antisymmetric stretching mode of O(2)H(2) and O(4)H(4) groups
				3684(85)	Symmetric stretching mode of O(2)H(2) and O(4)H(4) groups
		e	3620	3626(121)	Antisymmetric stretching mode of the O(1)H(1) and O(1)H(1') groups
	1B	g	3488	3519(48)	Symmetric stretching mode of the O(1)H(1) and O(1)H(1') groups
		b	3763	3762(175)	Stretching mode of the O(2)H(2) group
		c	3681	3702(81)	Antisymmetric stretching mode of O(3)H(3) and O(4)H(4) groups
				3709(131)	Symmetric stretching mode of O(3)H(3) and O(4)H(4) groups
		d	3660	3683(113)	Antisymmetric stretching mode of the O(1)H(1) and O(1)H(1') groups
		f	3546	3544(64)	Symmetric stretching mode of the O(1)H(1) and O(1)H(1') groups

^aIR intensities are listed in parentheses in km/mol, and the calculated harmonic vibrational frequencies are scaled by a factor of 0.948. The atom labelling is indicated in Figure 2.

**Figure 2.** Identified structures of neutral $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1-3$) (isomers 1A–3A and 1B–3B) clusters at the PBE0-D3(BJ)/def2-TZVP level of theory (O, red; H, light gray; Ta, dark blue). The atoms are labeled for discussion.

the theoretical spectrum of a single isomer (1A or 1B). The agreement between theory and experiment is achieved by mixing the theoretical spectra of 1A and 1B in a 1:1 ratio (Figure 1T₁), indicative of the coexistence of 1A and 1B, which is consistent with the small relative energy (within 0.5 kcal/mol) and large isomerization barrier. The experimental band a at 3781 cm^{-1} is assigned to the O(3)H(3) stretching vibration in isomer 1A (calculated: 3778 cm^{-1} ; Table 1). The shoulder band b at 3763 cm^{-1} corresponds to the O(2)H(2) stretch in isomer 1B (calculated: 3762 cm^{-1}). The adjacent intense feature c at 3681 cm^{-1} is attributed to the coupled stretching vibrations of O(4)H(4) and O(3)H(3) in isomer 1B (calculated: 3702 and 3709 cm^{-1}). The contribution of prominent band d at 3660 cm^{-1} comes from both isomers: in 1A, it arises from the overlapping stretches of O(4)H(4) and O(2)H(2) (calculated: 3680 and 3684 cm^{-1}); in 1B, it is primarily attributed to the antisymmetric stretching mode of the terminally coordinated water molecule's O(1)H(1)/O(1)H(1') groups (calculated: 3683 cm^{-1}). Band e at 3620 cm^{-1} is assigned to the antisymmetric stretch of the coordinated water molecule in 1A (O(1)H(1)/O(1)H(1')),

calculated: 3626 cm^{-1}). Band f at 3546 cm^{-1} matches the symmetric stretch of the same water moiety in 1B (calculated: 3544 cm^{-1}). Finally, band g at 3488 cm^{-1} is assigned to the symmetric stretch of the coordinated water in 1A (calculated: 3519 cm^{-1}).

The $\text{HTa}(\text{OH})_3$ core motif of the $n = 1$ cluster is retained in the larger clusters of $n = 2$ and 3, where additional water molecules bind via hydrogen bonding or terminal coordination. The largest isomerization barrier for $2\text{B} \rightarrow 2\text{A}$ and $3\text{B} \rightarrow 3\text{A}$ is predicted to be 6.2 and 6.9 kcal/mol at the CCSD(T)/def2-TZVPP level (Figure S7 and S8), respectively, indicative of unfavorable isomer interconversion in the cold molecular beam. A 1:1 mixture of the theoretical spectra of isomers 2A/2B and 3A/3B provides the best match to the corresponding experimental spectra (Figure S5b and S6b), suggesting the coexistence of isomers 2A/2B and 3A/3B. In the experimental spectrum of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_2$, the hydrogen bonded region ($2800-3460\text{ cm}^{-1}$) exhibits a broad envelope containing five distinguishable maxima. While static harmonic calculation predicts only two modes in the $2800-3460\text{ cm}^{-1}$ region (Figure 3b), the AIMD simulations successfully capture the

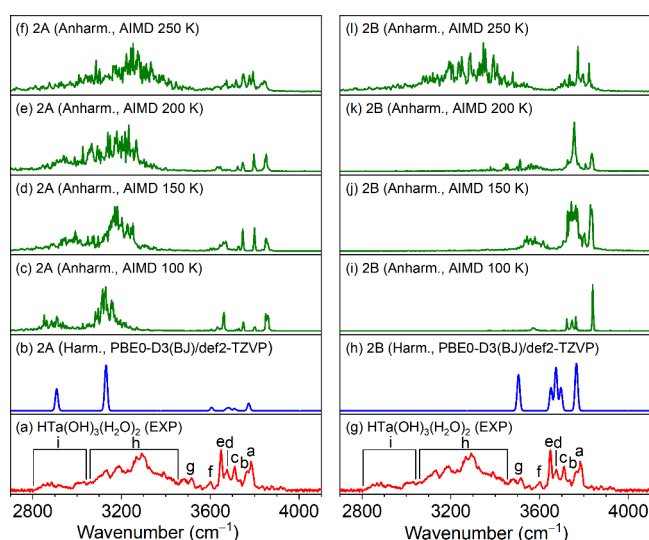


Figure 3. Comparison of experimental IR spectrum of neutral $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_2$ cluster (a, g), the PBE0-D3(BJ)/def2-TZVP calculated harmonic IR spectra of isomers 2A (b) and 2B (h), and AIMD spectra at 100, 150, 200, and 250 K of isomers 2A (c–f) and 2B (i–l). The units of experimental IR spectral intensities and AIMD simulated IR spectral intensities are a.u.; the units of PBE0-D3(BJ)/def2-TZVP calculated harmonic IR spectral intensities are km/mol .

spectral profiles (Figure 3d, *vide infra*). AIMD decomposition analysis shows that this splitting originates from the dynamic fluctuations of the $\text{O}(1)\cdots\text{H}(1)\cdots\text{O}(5)$ and $\text{O}(5)\cdots\text{H}(5')\cdots\text{O}(2)$ hydrogen bond network (Figure S9). Consequently, the bands in the $2800\text{--}3050\text{ cm}^{-1}$ region (labeled i) correspond to the coupled stretching vibration of the $\text{O}(1)\text{H}(1)$ group involved in strong water–water hydrogen bonds. The bands in the $3050\text{--}3460\text{ cm}^{-1}$ region (labeled h) are collectively assigned to the coupled stretching vibration mode dominated by $\text{O}(5)\text{H}(5')$. Detailed vibrational assignments for the $n = 2$ and 3 clusters are listed in Tables S2 and S3, respectively. In the experimental spectrum of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_3$, a weak band (labeled *) appears at 3864 cm^{-1} , for which quantum chemical and AIMD calculations yield no fundamental mode in this range. This feature is tentatively assigned to a combination band of an O–H stretching fundamental and a low-frequency water torsional vibration.^{37–39} The absence of the 3864 cm^{-1} band in the AIMD spectra could be due to the fact that the AIMD method intrinsically lacks the nuclear quantum effects that are required to reproduce multiquanta transitions.

The overall agreement between experiment and theory supports the structural assignments of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1\text{--}3$). As shown in Figure S10, the IR spectra of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 2\text{--}3$) are different from those of $\text{Ta}(\text{OH})_4(\text{H}_2\text{O})_m$ ($m = 1\text{--}2$), confirming the structural assignment of the $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ system. The studies on the $\text{Ta}(\text{OH})_4(\text{H}_2\text{O})_m$ system will be reported in a subsequent paper.

It can be seen from the above analyses that the static harmonic calculations cannot reproduce the spectral broadening of the bands in the hydrogen bonded region of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1\text{--}3$). Previous studies have shown that with the consideration of anharmonic effects, finite temperature effects, and hydrogen bonding dynamic behaviors, AIMD simulation is an effective theoretical approach to analyze the IR spectral broadening mechanism of flexible hydrogen bonded clusters.^{40–42} Therefore, we performed

AIMD simulations on the identified $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1\text{--}3$) structures. Considering that the spectral broadening becomes apparent at $n = 2$ and persists at $n = 3$, we focus on the discussion of AIMD simulated results for $n = 2$. The obtained AIMD spectra of $n = 2$ are shown in Figure 3, and those of $n = 1$ and 3 in Figures S11 and S12, respectively. For the $n = 1\text{--}3$ clusters, the simulated spectra at 150 K show best agreement with the experiment spectra, consistent with the estimated cluster temperature of $100\text{--}200\text{ K}$. It should be pointed out that since the AIMD simulation does not consider zero-point vibration and quantum nuclear effects, the simulation temperature does not strictly correspond to the experimental temperature.

The statistical analyses of hydrogen bond distance distributions for the representative $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_2$ cluster at different simulation temperatures are illustrated in Figure S13 and S14, respectively. As the temperature increases from 100 to 250 K, the peak of the hydrogen bond distance distribution shifts to longer distances and the distribution widens significantly (Figure S13e–h). For example, at 100 K the $\text{O}(1)\text{H}(1)\cdots\text{O}(5)$ hydrogen bond distance distribution for isomer 2A is concentrated mainly in the range $1.40\text{--}1.90\text{ \AA}$ (Figure S13e), with a peak of about $1.60\text{ \AA}$, while at 250 K the distribution extends to a wider range $1.30\text{--}2.50\text{ \AA}$ (Figure S13h), with a peak of about $1.70\text{ \AA}$. The blue shift of the peak indicates that thermal motion weakens the average strength of hydrogen bonds, while the broadening of the distribution quantitatively reveals an increase in the dynamic disorder of the hydrogen bond network. Such thermally driven expansion of the instantaneous hydrogen bond conformations is the structural origin of the broadened hydrogen bonded O–H stretching bands, and it reproduces the relative widths of the experimental bands (e.g., band h vs i; Figure 3a).

To discuss the hydrogen bond (HB) strengths, we consider both the oxygen–oxygen distance ($R_{\text{O}\cdots\text{O}}$) and the dynamical stability. As detailed in the comprehensive review by Steiner,⁴³ decreasing the donor–acceptor distance is associated with a systematic increase in bond enthalpy and covalent character. In the context of our clusters, considering that typical water–water H-bonds have distances of $\sim 2.83\text{ \AA}$,⁴³ we distinguish interactions with $R_{\text{O}\cdots\text{O}} < 2.65\text{ \AA}$ as being significantly stronger and more covalent in character, while classifying those with longer distances or large thermal fluctuations as “weak” or fluxional.

In isomer 2A, the $\text{O}(5)\cdots\text{O}(2)$ and $\text{O}(1)\cdots\text{O}(5)$ bonds have short static distances of $2.61\text{ \AA}$ and $2.58\text{ \AA}$, respectively, falling into the “strong” HB regime. At 150 K, the change amplitude of the $\text{O}(5)\text{H}(5')\cdots\text{O}(2)$ hydrogen bond distance of isomer 2A (Figure S13b, $\sim 0.8\text{ \AA}$) is greater than that of $\text{O}(1)\text{H}(1)\cdots\text{O}(5)$ (Figure S13f, $\sim 0.6\text{ \AA}$), resulting in a wider broadening of the $\text{O}(5)\text{H}(5')$ stretching mode as compared to the latter. This is consistent with the experimental result that band h is wider than band i (Figure 3a,g). In addition, although the $\text{O}(1)\cdots\text{O}(4)$ bond has a short static distance ($2.56\text{ \AA}$) due to steric constraints, it exhibits high fluxionality. At 150 K, the $\text{O}(1)\text{H}(1')\cdots\text{O}(4)$ hydrogen bond distance changes in the range of $1.70\text{--}3.20\text{ \AA}$ (amplitude $\sim 1.5\text{ \AA}$) (Figure S13j), which is significantly larger than those of other hydrogen bonds, indicating that its dynamical strength is weaker. This is consistent with the frequency of the experimental band f being higher than bands h and i (Figure 3a,g).

For isomer 2B, the HB network is asymmetric, featuring a notably longer bond ($R_{\text{O}(5)\cdots\text{O}(4)} = 2.80\text{ \AA}$) alongside a shorter

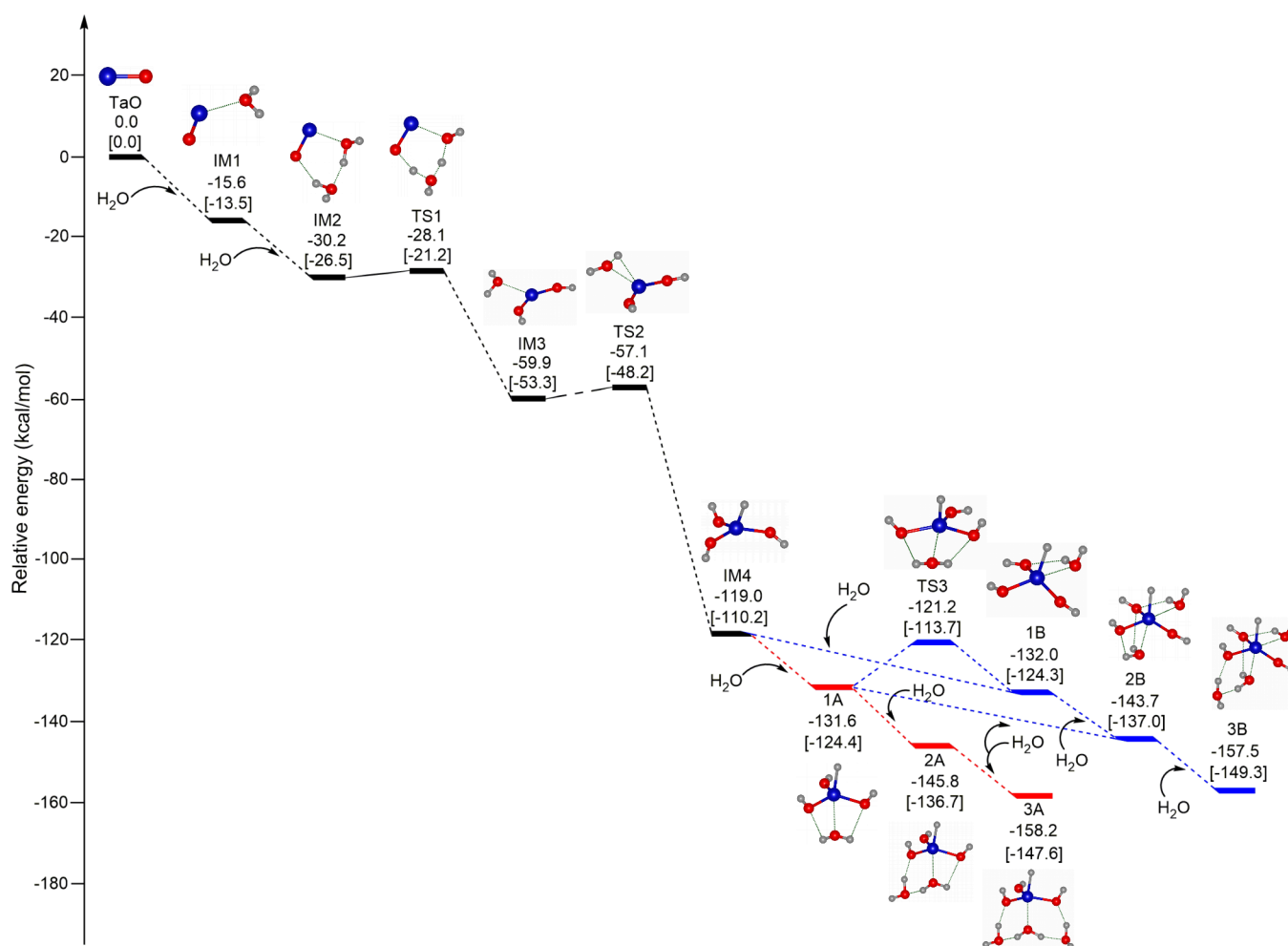


Figure 4. Potential energy profiles of pathway I for the formation of $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1-3$) (isomers 1A–3A and 1B–3B). Relative energies calculated at the PBE0-D3(BJ)/def2-TZVP and CCSD(T)/def2-TZVPP (in square brackets) level of theory are listed in kcal/mol. The abbreviation “IM” stands for intermediate and “TS” for transition state. The corresponding structures are embedded in the inset (O, red; H, light gray; Ta, dark blue).

one ($R_{\text{O}(5)\cdots\text{O}(3)} = 2.60 \text{ \AA}$). Consequently, the hydrogen bond distance distribution of $\text{O}(5)\text{H}(5')\cdots\text{O}(4)$ and $\text{O}(5)\text{H}(5')\cdots\text{O}(3)$ of isomer 2B (Figure S14b,f) shows a double peak starting from 150 K. This is because the network contains this weak link ($2.80 \text{ \AA}$), allowing the coordinated water molecules repeatedly flip over at 150 K, that is, the labile $\text{O}(5)\text{H}(5')\cdots\text{O}(4)$ bond is broken and a new hydrogen bond $\text{O}(5)\text{H}(5')\cdots\text{O}(2)$ is formed with $\text{O}(2)$. The coexistence of different OH vibrational frequencies further explains the broadening and complex peak shapes in this region in the experimental and simulated spectra.

Given the inherent complexity of reaction processes in laser vaporization sources and the associated challenges in characterizing transient intermediates, quantum chemical calculations were used to explore the possible formation mechanisms of the $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ ($n = 1-3$) products. Considering that the TaO^+ signal is a major mass peak in the mass spectrum (Figure S2), we focus on the reaction pathways initiating from TaO. From a stoichiometric perspective, this choice matches the target structural core, $\text{HTa}(\text{OH})_3$ (i.e., TaO_3H_4), which corresponds directly to the addition of two water molecules to TaO. Alternative precursors, such as higher oxides (e.g., TaO_2), are stoichiometrically incompatible without invoking complex fragmentation steps. Furthermore, previous studies

established that the reaction $\text{Ta} + \text{H}_2\text{O} \rightarrow \text{TaO} + \text{H}_2$ is thermodynamically exothermic.²² While this H_2 elimination channel is kinetically hindered in cryogenic matrices,²² the high temperatures generated in the laser ablation plasma readily overcome it, naturally funneling any bare Ta atoms into the TaO species. Thus, TaO acts as a thermodynamically stable initial building block for the subsequent clustering and hydrolysis processes. Regarding the subsequent reaction steps, our experimental and theoretical focus centers on the solvated $\text{HTa}(\text{OH})_3(\text{H}_2\text{O})_n$ clusters due to intrinsic kinetic and spectroscopic constraints. Accordingly, three possible formation pathways initiating from TaO are shown in Figures 4, S15, and S16, respectively, with thermodynamic data in Tables S4–S6. The CCSD(T)/def2-TZVPP-calculated energies are used for the following discussion of formation pathways.

As shown in Figure 4 (pathway I), following the exothermic formation of intermediate 1 (IM1) (-13.5 kcal/mol), the second water molecule assembles via hydrogen bonding to form a six-membered cyclic intermediate, IM2, releasing an additional 12.9 kcal/mol . Significantly, this cyclic structure enables a subsequent hydrogen transfer through a six-membered cyclic transition state (TS1) with a small barrier of 5.3 kcal/mol , leading to IM3 with a heat release of 26.9 kcal/mol . The $\text{IM3} \rightarrow \text{IM4}$ isomerization is a highly

exothermic step (56.9 kcal/mol) with a small barrier (5.1 kcal/mol) and yields the core species HTa(OH)₃. Water then binds at different site of IM4 to form isomer 1A (Figure 4, red curve) or isomer 1B (Figure 4, blue curve). With successive addition of H₂O, isomers 2A/2B and 3A/3B are formed. All the HTa(OH)₃(H₂O)_n (*n* = 1–3) formation processes from the HTa(OH)₃ hydration are exothermic (11–15 kcal/mol).

We tried IR-VUV measurements of the TaO₃H₄ species. However, no IR depletion signal was observed. As analyzed above, the sequential transformation from the hydrogen bonded cyclic IM2 to the final product IM4 via TS1 and TS2 features low barriers and high exothermicity. In the high-collision environment prior to supersonic expansion, the transient intermediate (IM2) rapidly relaxes into the global minimum (IM4). At the PBE0-D3(BJ)/def2-TZVP level, the lowest dissociation energies of IM4, corresponding to the loss of the Ta-bound H atom or an OH group, are 2.81 and 5.31 eV, respectively. These dissociation thresholds vastly exceed the energy of a single IR photon (0.21–0.46 eV in the 1700–3700 cm^{−1} region). Since IM4 lacks weakly bound solvent molecules, it does not readily undergo vibrational photo-dissociation with the tabletop IR light source, which prevents the IR-VUV spectral measurements of the TaO₃H₄ species.

For pathway II (Figure S15), the IM1 → IM2 isomerization is exothermic by 60.1 kcal/mol with a barrier of 10.5 kcal/mol.²⁵ Addition of the second water molecule yields IM3 (exothermic by 21.0 kcal/mol), but its subsequent isomerization to IM4 requires a substantially higher barrier of 17.1 kcal/mol, rendering this route kinetically less favorable. Similarly, in pathway III (Figure S16), where the second water molecule coordinates directly to the metal center of IM1 to form a noncyclic structure IM2, the initial isomerization to IM3 has a moderate barrier of 7.1 kcal/mol and the subsequent isomerization to IM4 also encounters a larger barrier of 17.1 kcal/mol.

All three pathways are thermodynamically exothermic and kinetically feasible for generating the HTa(OH)₃ core. However, pathway I is the dominant route due to its kinetics: the hydrogen transfer through the six-membered hydrogen bond network proceeds with a barrier of only 5.3 kcal/mol, far lower than the highest barriers of 17.1 kcal/mol in pathways II and III. To elucidate the microscopic driving forces behind this kinetic advantage, the evolution of chemical bonding and electronic structures along pathway I was discussed by Wiberg bond indices (WBI) and Natural Population Analysis (NPA) (Figure S17 and Tables S7–S8). Initially, the formation of the hydrogen bond network (IM2) induces a ligand-to-metal charge transfer, polarizing the terminal oxo ligand O(2) (its natural charge reaches −0.855) to prime it as a strong proton acceptor. During the concerted proton relay in TS1, the WBI captures the transient “half-broken/half-formed” nature of the participating bonds, driving the complete activation of the original Ta = O double bond into a single Ta–OH linkage in IM3 (WBI drops from ~1.97 to 0.90). Significantly, the deep cleavage of the second water molecule in TaO(H₂O)_n (via TS2) unveils a distinct oxidative addition mechanism. Upon generating the final HTa(OH)₃ core (IM4), the transferring hydrogen abruptly shifts from a protic state (charge ~ +0.50) to a hydridic state (charge −0.228), accompanied by the deep oxidation of the Ta center. Thus, pathway I is kinetically most conducive to the efficient production of the target products. Conversely, without this cooperative network, the dissociation of a single water molecule on TaO is kinetically hindered by

these substantially higher barriers. These findings highlight the pivotal role of the hydrogen bond network in lowering the reaction barrier, which substantiates the hydrogen bonding effects proposed on metal oxide surfaces, metal organic frameworks, and zeolites.^{5,6,44} Coincidentally, one-dimensional hydrogen bonds in water chains inhibit the water dissociation reaction on TiO₂ surfaces, whereas a single hydrogen bond in a water dimer remarkably enhances the OH dissociation.⁵ These results would have important implications for developing efficient catalysts via the regulation of local environments.

In summary, neutral products from the tantalum–water reactions were spectroscopically characterized by combining the size-specific IR-VUV technique with quantum chemical calculations and AIMD simulations. The spectral fingerprints reveal the formation of a metal hydride core, HTa(OH)₃, which is solvated by a cooperative water network to form the HTa(OH)₃(H₂O)_n (*n* = 1–3) products. For the *n* = 1 solvated species, the water molecule stabilizes the core via a cyclic hydrogen bond motif, while larger clusters (*n* = 2 and 3) evolve into the extended hydrogen bond networks. The AIMD simulations disentangle the significant dynamic fluxionality of these solvent shells and provide a microscopic explanation for the characteristic broadening observed in the experimental spectra. Mechanistic studies show that the formation of the HTa(OH)₃ core is driven by a water-assisted hydrolysis pathway, in which the second water molecule in TaO(H₂O)_n effectively lowers the reaction energy barrier through the six-membered hydrogen bond network. Chemical bonding and charge analyses along the TaO + 2H₂O → HTa(OH)₃ reactions afford chemical insights for this water splitting reaction. This work provides molecular-level insight into the mechanism of water decomposition on metals and bridges the gap between gas-phase and condensed-phase chemistry of metal–water interactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.6c01999>.

Detailed experimental and theoretical methods; infrared pulse energy curve (Figure S1); mass spectrum (Figure S2); comparison of experimental IR spectra of *n* = 1 under different experimental conditions (Figure S3); comparison of experimental and calculated IR spectra of HTa(OH)₃(H₂O)_n (*n* = 1–3) (Figures S4–S6); potential energy profiles for the isomerization between isomers *n*A and *n*B (*n* = 2–3) (Figures S7–S8); dipole time-correlation function spectrum and density of state plots of isomer 2A (Figure S9); comparison of experimental IR spectra of HTa(OH)₃(H₂O)_n (*n* = 2–3) and Ta(OH)₄(H₂O)_m (*m* = 1–2) (Figure S10); AIMD simulated infrared spectra (Figures S11–S12); hydrogen bond distance distribution (Figures S13–S14); potential energy profiles and reaction energies of the formation of HTa(OH)₃(H₂O)_n (*n* = 1–3) complexes (Figures S15–S16); optimized structures of the key species along pathway I (Figure S17); calculated vertical ionization potentials for the isomers (Table S1); comparison of experimental band positions of HTa(OH)₃(H₂O)_n (*n* = 2–3) to the calculated values of the most stable structures (Tables S2–S3); reaction energies of pathways I–III for the formation of HTa–

(OH)₃(H₂O)_n (*n* = 1–3) (Tables S4–S6); natural charges (Table S7) and bond lengths/wiberg bond indices (Table S8) of the key species along pathway I; Cartesian coordinates of the isomers, intermediates, and transition states; and supporting references (PDF)

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Notes

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REFERENCES

- (1) Mu, R.; Zhao, Z. J.; Dohnalek, Z.; Gong, J. Structural Motifs of Water on Metal Oxide Surfaces. *Chem. Soc. Rev.* **2017**, *46*, 1785–1806.
- (2) Zhang, P.; Zhang, J.; Gong, J. Tantalum-Based Semiconductors for Solar Water Splitting. *Chem. Soc. Rev.* **2014**, *43*, 4395–4422.
- (3) Elsayed, N.; El-Rabiei, M. M.; Negem, M.; Heakal, F. E.-T. The Potential of Tantalum as an Efficient Electrocatalyst for Green Hydrogen Production. *Electrochim. Acta* **2022**, *404*, 139783.
- (4) Han, C.; Wang, T. Understanding the Catalytic Performances of Metal-Doped Ta₂O₅ Catalysts for Acidic Oxygen Evolution Reaction with Computations. *Chem. Sci.* **2024**, *15*, 14371–14378.
- (5) Yang, W.; Wei, D.; Jin, X.; Xu, C.; Geng, Z.; Guo, Q.; Ma, Z.; Dai, D.; Fan, H.; Yang, X. Effect of the Hydrogen Bond in Photoinduced Water Dissociation: A Double-Edged Sword. *J. Phys. Chem. Lett.* **2016**, *7*, 603–608.
- (6) Grifoni, E.; Piccini, G.; Lercher, J. A.; Glezakou, V. A.; Rousseau, R.; Parrinello, M. Confinement Effects and Acid Strength in Zeolites. *Nat. Commun.* **2021**, *12*, 2630.
- (7) Wang, A.; Li, J.; Zhang, T. Heterogeneous Single-Atom Catalysis. *Nat. Rev. Chem.* **2018**, *2*, 65–81.
- (8) Guo, Q.; Ma, Z.; Zhou, C.; Ren, Z.; Yang, X. Single Molecule Photocatalysis on TiO₂ Surfaces. *Chem. Rev.* **2019**, *119*, 11020–11041.
- (9) Weichman, M. L.; Debnath, S.; Kelly, J. T.; Gewinner, S.; Schöllkopf, W.; Neumark, D. M.; Asmis, K. R. Dissociative Water Adsorption on Gas-Phase Titanium Dioxide Cluster Anions Probed with Infrared Photodissociation Spectroscopy. *Top. Catal.* **2018**, *61*, 92–105.
- (10) Wang, T.-H.; Fang, Z.; Gist, N. W.; Li, S.; Dixon, D. A.; Gole, J. L. Computational Study of the Hydrolysis Reactions of the Ground and First Excited Triplet States of Small TiO₂ Nanoclusters. *J. Phys. Chem. C* **2011**, *115*, 9344–9360.
- (11) Sambrano, J. R.; Andrés, J.; Gracia, L.; Safont, V. S.; Beltrán, A. DFT Study of the Water-Assisted Tautomerization Process between

Hydrated Oxide, $\text{MO}(\text{H}_2\text{O})^+$, and Dihydroxide, $\text{M}(\text{OH})_2^+$, Cations ($\text{M} = \text{V}, \text{Nb}$ and Ta). *Chem. Phys. Lett.* **2004**, *384*, 56–62.

- (12) Xu, H. G.; Li, X. N.; Kong, X. Y.; He, S. G.; Zheng, W. J. Interaction of TiO^+ with Water: Infrared Photodissociation Spectroscopy and Density Functional Calculations. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17126–17133.
- (13) Chen, Y.; Jin, J.; Xin, K.; Yu, W.; Xing, X.; Wang, X.; Wang, G. Infrared Photodissociation Spectroscopic Studies of $\text{ScO}(\text{H}_2\text{O})_{n=1-3}\text{Ar}^+$ Cluster Cations: Solvation Induced Reaction of ScO^+ and Water. *Phys. Chem. Chem. Phys.* **2019**, *21*, 15639–15646.
- (14) Xin, K.; Chen, Y.; Zhang, L.; Xu, B.; Wang, X.; Wang, G. Infrared Photodissociation Spectroscopic Investigation on VO^+ and NbO^+ Hydrolysis Catalyzed by Water Molecules. *Phys. Chem. Chem. Phys.* **2021**, *23*, 528–535.
- (15) Heller, J.; Pascher, T. F.; van der Linde, C.; Oncák, M.; Beyer, M. K. Photochemical Hydrogen Evolution at Metal Centers Probed with Hydrated Aluminium Cations, $\text{Al}^+(\text{H}_2\text{O})_n$, $n = 1-10$. *Chem.—Eur. J.* **2021**, *27*, 16367–16376.
- (16) Heller, J.; Tang, W. K.; Cunningham, E. M.; Demissie, E. G.; van der Linde, C.; Lam, W. K.; Oncák, M.; Siu, C. K.; Beyer, M. K. Getting Ready for the Hydrogen Evolution Reaction: The Infrared Spectrum of Hydrated Aluminum Hydride-Hydroxide $\text{HAL-OH}^+(\text{H}_2\text{O})_{n-1}$, $n = 9-14$. *Angew. Chem., Int. Ed.* **2021**, *60*, 16858–16863.
- (17) Jian, X.; Xin, K.; Hu, J.; Zhang, L.; Wang, X.; Wang, G. Infrared Spectroscopy of Solvation in the TaO_2^+ Hydrolysis Reaction. *J. Phys. Chem. A* **2021**, *125*, 5054–5060.
- (18) Madlener, S. J.; Yuan, B.; Reimann, M.; Zhou, S.; Beyer, M. K.; Bakker, J. M.; van der Linde, C. Infrared Multiple Photon Dissociation Spectroscopy of $\text{TaO}(\text{OH})_2^+$ and $\text{Ta}(\text{OH})_4^+$ Cations. *Int. J. Mass Spectrom.* **2026**, *519*, 117543.
- (19) Lange, K.; Visser, B.; Neuwirth, D.; Eckhard, J. F.; Boesl, U.; Tschurl, M.; Bowen, K. H.; Heiz, U. Size-Dependent Gas Phase Reactivity of Tantalum Cluster Cations with Small Alcohols. *Int. J. Mass Spectrom.* **2015**, *375*, 9–13.
- (20) Santos, M.; Michelini, M. d. C.; Lourenço, C.; Marçalo, J.; Gibson, J. K.; Oliveira, M. C. Gas-Phase Oxidation Reactions of Ta_2^+ : Synthesis and Properties of TaO_2^+ and TaO_2^{2+} . *J. Phys. Chem. A* **2012**, *116*, 3534–3540.
- (21) Zhou, M.; Zhang, L.; Dong, J.; Qin, Q. Reactions of Group IV Metal Atoms with Water Molecules. Matrix Isolation FTIR and Theoretical Studies. *J. Am. Chem. Soc.* **2000**, *122*, 10680–10688.
- (22) Zhou, M.; Dong, J.; Zhang, L.; Qin, Q. Reactions of Group V Metal Atoms with Water Molecules. Matrix Isolation FTIR and Quantum Chemical Studies. *J. Am. Chem. Soc.* **2001**, *123*, 135–141.
- (23) Zhang, L.; Dong, J.; Zhou, M. Matrix-Isolation Fourier Transform Infrared and Theoretical Studies of Laser-Ablated Sc Atom Reactions with Water Molecules. *J. Phys. Chem. A* **2000**, *104*, 8882–8886.
- (24) Zhang, L.; Shao, L.; Zhou, M. Reactions of Laser-Ablated Y and La Atoms with H_2O Infrared Spectra and Density Functional Calculations of the HMO , HMOH and $\text{M}(\text{OH})_2$ Molecules in Solid Argon. *Chem. Phys.* **2001**, *272*, 27–36.
- (25) Zhou, M.; Zhuang, J.; Wang, G.; Chen, M. Matrix Isolation Spectroscopic and Theoretical Study of Water Adsorption and Hydrolysis on Molecular Tantalum and Niobium Oxides. *J. Phys. Chem. A* **2011**, *115*, 2238–2246.
- (26) Romanini, D.; Biennier, L.; Salama, F.; Kachanov, A.; Allamandola, L. J.; Stoeckel, F. Jet-Discharge Cavity Ring-Down Spectroscopy of Ionized Polycyclic Aromatic Hydrocarbons: Progress in Testing the PAH Hypothesis for the Diffuse Interstellar Band Problem. *Chem. Phys. Lett.* **1999**, *303*, 165–170.
- (27) Dinu, D. F.; Podewitz, M.; Grothe, H.; Loerting, T.; Liedl, K. R. On the Synergy of Matrix-Isolation Infrared Spectroscopy and Vibrational Configuration Interaction Computations. *Theor. Chem. Acc.* **2020**, *139*, 174.
- (28) Vlahos, K.; DeWitt, M.; Neumark, D. M. High-Resolution Photoelectron Spectroscopy of Cryogenically Cooled VO_3H_2^- . *J. Phys. Chem. A* **2026**, *130*, 3037–3047.
- (29) Abou Taka, A.; Babin, M. C.; Sheng, X.; DeVine, J. A.; Neumark, D. M.; Hratchian, H. P. Unveiling the Coexistence of Cis- and Trans-Isomers in the Hydrolysis of ZrO_2 : A Coupled DFT and High-Resolution Photoelectron Spectroscopy Study. *J. Chem. Phys.* **2020**, *153*, 244308.
- (30) DeVine, J. A.; Abou Taka, A.; Babin, M. C.; Weichman, M. L.; Hratchian, H. P.; Neumark, D. M. High-Resolution Photoelectron Spectroscopy of TiO_3H_2^- : Probing the $\text{TiO}_2^- + \text{H}_2\text{O}$ Dissociative Adduct. *J. Chem. Phys.* **2018**, *148*, 222810.
- (31) Weichman, M. L.; Neumark, D. M. Slow Photoelectron Velocity-Map Imaging of Cryogenically Cooled Anions. *Annu. Rev. Phys. Chem.* **2018**, *69*, 101–124.
- (32) Bauschlicher, C. W.; Jacobson, N. S.; Myers, D. L. Quantum Chemical Calculations of the Thermochemistry of Tantalum Oxyhydroxide Species. *J. Am. Ceram. Soc.* **2019**, *102*, 3836–3842.
- (33) Hu, J.; Shi, S.; Lei, D.; Duan, Z.; Jiang, J.; Tang, L.; Chen, D. Based on Density Functional Theory: Reactions Mechanism of Ta_n ($n = 2-5$) Clusters and Water Molecules. *Comput. Theor. Chem.* **2023**, *1229*, 114351.
- (34) Zhang, B. B.; Yu, Y.; Zhang, Z. J.; Zhang, Y. Y.; Jiang, S. K.; Li, Q. M.; Yang, S.; Hu, H. S.; Zhang, W. Q.; Dai, D. X.; Wu, G. R.; Li, J.; Zhang, D. H.; Yang, X. M.; Jiang, L. Infrared Spectroscopy of Neutral Water Dimer Based on a Tunable Vacuum Ultraviolet Free Electron Laser. *J. Phys. Chem. Lett.* **2020**, *11*, 851–855.
- (35) Zheng, H. J.; Jiang, S.; Yan, W. H.; Wang, T. T.; Li, S. D.; Xie, H.; Li, G.; Yang, X. M.; Jiang, L. Size-Specific Infrared Spectroscopic Study of the Reactions between Water Molecules and Neutral Vanadium Dimer: Evidence for Water Splitting. *J. Phys. Chem. Lett.* **2023**, *14*, 3878–3883.
- (36) Li, G.; Xie, H.; Jiang, L. Size-specific infrared spectroscopy of neutral hydrated clusters based on a vacuum ultraviolet free electron laser. *J. Phys. Chem. Lett.* **2024**, *15*, 4806–4814.
- (37) Altman, R. M.; Richmond, G. L. Twist and Stretch: Assignment and Surface Charge Sensitivity of a Water Combination Band and Its Implications for Vibrational Sum Frequency Spectra Interpretations. *J. Phys. Chem. B* **2021**, *125*, 6717–6726.
- (38) Carnegie, P. D.; McCoy, A. B.; Duncan, M. A. IR Spectroscopy and Theory of $\text{Cu}^+(\text{H}_2\text{O})\text{Ar}_2$ and $\text{Cu}^+(\text{D}_2\text{O})\text{Ar}_2$ in the O-H (O-D) Stretching Region: Fundamentals and Combination Bands. *J. Phys. Chem. A* **2009**, *113*, 4849–4854.
- (39) Doublerly, G. E.; Walters, R. S.; Cui, J.; Jordan, K. D.; Duncan, M. A. Infrared Spectroscopy of Small Protonated Water Clusters, $\text{H}^+(\text{H}_2\text{O})_n$ ($n = 2-5$): Isomers, Argon Tagging, and Deuteration. *J. Phys. Chem. A* **2010**, *114*, 4570–4579.
- (40) Jiang, S. K.; Su, M. Z.; Yang, S.; Wang, C.; Huang, Q. R.; Li, G.; Xie, H.; Yang, J. Y.; Wu, G. R.; Zhang, W. Q.; Zhang, Z. J.; Kuo, J. L.; Liu, Z. F.; Zhang, D. H.; Yang, X. M.; Jiang, L. Vibrational Signature of Dynamic Coupling of a Strong Hydrogen Bond. *J. Phys. Chem. Lett.* **2021**, *12*, 2259–2265.
- (41) Jiang, L.; Sun, S. T.; Heine, N.; Liu, J. W.; Yacovitch, T. I.; Wende, T.; Liu, Z. F.; Neumark, D. M.; Asmis, K. R. Large Amplitude Motion in Cold Monohydrated Dihydrogen Phosphate Anions $\text{H}_2\text{PO}_4^-(\text{H}_2\text{O})$: Infrared Photodissociation Spectroscopy Combined with Ab Initio Molecular Dynamics Simulations. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1314–1318.
- (42) Sun, S. T.; Jiang, L.; Liu, J. W.; Heine, N.; Yacovitch, T. I.; Wende, T.; Asmis, K. R.; Neumark, D. M.; Liu, Z. F. Microhydrated Dihydrogen Phosphate Clusters Probed by Gas Phase Vibrational Spectroscopy and First Principles Calculations. *Phys. Chem. Chem. Phys.* **2015**, *17*, 25714–25724.
- (43) Steiner, T. The Hydrogen Bond in the Solid State. *Angew. Chem., Int. Ed.* **2002**, *41*, 48–76.
- (44) Zuluaga, S.; Fuentes-Fernandez, E. M. A.; Tan, K.; Li, J.; Chabal, Y. J.; Thonhauser, T. Cluster Assisted Water Dissociation Mechanism in MOF-74 and Controlling It Using Helium. *J. Mater. Chem. A* **2016**, *4*, 11524–11530.