Observation of Surface-Bound Negatively Charged Hydride and Hydroxide on GaP(110) in H₂O Environments

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ABSTRACT: Surface-bound species on GaP(110) formed upon interaction with water were investigated through experiment and theory. These studies are motivated by and discussed in the context of electrocatalytic and photoelectrocatalytic schemes for solar fuel production, including especially observations of selective CO₂ reduction to methanol in acidified aqueous solutions of CO₂ and nitrogen-containing heteroaromatics. Experimentally, surface-bound species over 10 orders of magnitude of pressure were spectroscopically identified in situ using synchrotron-based ambient pressure photoelectron spectroscopy. Ga 3d and O 1s core-level spectra indicate that the interaction of GaP(110) with H₂O induces formation of a partially dissociated adlayer, characterized by the presence of both Ga−OH and molecular H₂O species. Measurements of the P 2p core level indicate formation of a negatively charged hydride that irreversibly bonds to surface P in vacuum. The surface densities of the hydroxide and hydride species increase with increasing pressure (surface coverage) of water. Periodic slab calculations using density functional theory were used to study several relevant water configurations at 298 K on this surface. Consistent with earlier theoretical predictions at 0 K, the calculations confirm that Ga−OH, molecular H₂O, and P−H species are thermodynamically stable on the GaP(110) surface under experimental conditions. Isobaric measurements at elevated pressures were used to probe the thermal stabilities of adsorbed species as well as the oxidation of surface Ga and P. The observation of stable surface hydride formation induced by interaction with water is especially notable given the critical role of hydride transfer to catalysts and CO₂ during chemical fuel synthesis reactions in aqueous environments. It is hypothesized that the observed high stability of the hydride on GaP may contribute to its associated remarkable near-100% faradaic efficiency for methanol generation by solar-driven CO₂ reduction in acidified aqueous pyridine solutions [J. Am. Chem. Soc. 2008, 130, 6342] because such stability is known to yield high overpotentials for the competing hydrogen evolution reaction.

1. INTRODUCTION

Developing an efficient technology to create liquid fuels from renewable energy sources represents one of the greatest technical challenges facing society. Solar-driven electro-reduction of CO₂ to carbon-containing fuels is a promising strategy because photoelectrocatalysis can facilitate the energy conversion and charge-transfer processes necessary for these endergonic chemical bond transformations to occur. Ideally, a catalyzed CO₂ reduction process will produce liquid fuels that can be stored on a large scale and utilized subsequently in a carbon-neutral cycle. In order to yield useful products and to occur at reasonable potentials (e.g., enabled by solar energy), electrochemical CO₂ reduction requires the transfer of multiple electrons and protons in a concerted manner, as occurs in nature. A particularly noteworthy and promising CO₂ reduction system was described in a recent study from Bocarsly and co-workers, which reported highly selective solar-driven photoelectrocatalytic reduction of CO₂ to methanol at p-type GaP photocathodes in pyridine(Py)-containing acidified aqueous solutions at cathodic underpotential. Electrochemical CO₂ reduction experiments with other electrode surfaces have been reported, but high faradaic efficiency toward methanol (near 100%) is observed only when using p-GaP, and more recently with p-CulnS₂ electrodes.

Following the initial report of photoelectrocatalytic CO₂ reduction with GaP, Bocarsly and co-workers suggested a homogeneous mechanism for the photoelectrochemical reduc-
tion of CO₂ catalyzed by pyridinium (for the reported conditions of pH = 5.2, approximately half of the Py is in the protonated form pyridinium, PyH⁺). In this postulated mechanism, the first step consists of the one-electron reduction of PyH⁺ to the aqueous pyridyl radical (PyH*). In the second step, PyH* reacts with CO₂ to form a carbamate complex. The validity of this mechanism was later disproved by computational studies,⁹–¹² which report that the calculated reduction potential for the homogeneous reduction of PyH⁺ to PyH* (∼−1.4 V vs. SCE) is much more negative than the experimentally observed potential.¹³ In addition, the pKₐ of PyH⁺ was found to be ∼27 in theoretical studies,¹⁰¹¹ which suggests that formation of the carbamate species is unlikely to occur, as it would require at least partial deprotonation of the PyH* radical in the transition state.

Recent theoretical studies of the relative stability of water- and Py-derived species in solution and adsorbed on GaP(110) led to the hypothesis of an alternative heterogeneous mechanism for CO₂ reduction involving adsorbed nitrogen heterocycles.¹³–¹⁷ These studies motivated our present investigation of the interaction of water with GaP(110). Specifically, a report by Muñoz-García and Carter¹³ considered the interaction between water and GaP(110) at 0 K. They predicted that water dissociation is thermodynamically favored on this surface and produces hydride-like species adsorbed on phosphorus sites along with water and hydroxyl bound to gallium sites. Following this work, Keith and Carter¹⁴ predicted that dihydropyridine (DHP) could exist in solution under the electrochemical conditions of the Bocarsly experiments. In particular, the authors determined that the homogeneous two-electron reduction potential of Py to DHP, Py + 2H⁺ + 2e⁻ → DHP, is ∼−0.72 V versus SCE,¹⁴ which is close to the applied operating potential. However, homogeneous DHP, like homogeneous PyH⁺, was ruled out as an electrocatalyst because of high predicted barriers for CO₂ insertion to form carbamate. Therefore, on the basis of the predicted phosphorus-bound hydride species induced by dissociation of water mentioned above,¹³ Keith and Carter¹⁴,¹⁵ hypothesized that adsorbed Py could be reduced to DHP on GaP(110) by adsorbed hydride-like species and protons in solution. Keith et al.¹⁶ also predicted the stable adsorption of both Py and DHP on the GaP(110) surface at room temperature, which supports the idea that the two-electron reduction of Py should occur on the surface prior to further catalytic reduction of CO₂.

Alternative mechanisms for the reduction of CO₂ catalyzed by Py-derived species have been proposed. In a mechanism suggested by Batista and co-workers¹² relevant for Pt electrodes, PyH⁺ is reduced to Py, resulting in adsorbed hydride; in a subsequent step, the surface hydride is transferred to the CO₂ molecule together with a proton from PyH⁺ to produce formic acid. Although this mechanism can explain experimental observations on Pt and features low activation barriers, the nagging question remains as to why PyH⁺ is required, given that this mechanism invokes only PyH⁺ as a proton donor; therefore, any Bronsted acid of similar acidity should be sufficient to reduce CO₂. However, this is not the case; only nitrogen heterocycles have been effective as cocatalysts. Recently, an alternative homogeneous mechanism involving DHP was suggested.¹⁸ However, a homogeneous mechanism cannot explain the significant electrode dependence of the catalysis, namely why underpotentials and high selectivity are observed only at certain electrodes.

In summary, thus far only the proposed mechanism involving adsorbed hydrides¹³ and adsorbed DHP¹⁴–¹⁷ is consistent with experimental observations and theoretical predictions made on GaP. First, experiments show that Py-derived species are required for this catalysis and that the product yield heavily favoring methanol is unique to GaP — hence adsorbed intermediates are involved.⁴⁵ Second, theoretical calculations predict that the hypothetical PyH⁺ adsorbed on GaP(110) spontaneously ionizes to form PyH⁺, which then would immediately desorb as it strongly prefers to exist in aqueous solution.¹⁶ Thus, in addition to homogeneous PyH⁺ being excluded as the active cocatalyst,⁹–¹² adsorbed PyH⁺ and PyH⁺ are also ruled out, leaving DHP as the most likely adsorbate involved.¹⁵–¹⁷ However, no direct observation of intermediates on GaP has been reported as yet. Herein, we experimentally investigate the interaction of water with GaP(110) to begin interrogation of this mechanism. We use ambient pressure photoelectron spectroscopy (APPES) to follow the O 1s, Ga 3d, and P 2p core levels to study the interaction of water with GaP(110) over 10 orders of magnitude of pressure. Via measurements of the P 2p level, we observe formation of a negatively charged hydride that irreversibly bonds to surface P on GaP(110), consistent with earlier theoretical predictions.¹³ The measurements confirm that Ga−OH and molecular H₂O exist on this surface in the presence of water.¹⁷ We also report further density functional theory (DFT) calculations that consider relevant water configurations on the GaP(110) surface and their thermodynamic stabilities at room temperature. Experimental observations of the hydride species afford further analysis and discussion herein on the role of surface hydrides in selectively catalyzing CO₂ reduction.

2. EXPERIMENTAL PROCEDURES

2.1. Ambient Pressure Photoelectron Spectroscopy. In situ APPES (or high-pressure X-ray photoelectron spectroscopy (HP-XPS)) experiments were performed at beamline X1A1 at the National Synchrotron Light Source (NSLS). The system¹⁹ operates over a wide range of pressures through use of a differentially pumped hemispherical analyzer (Specs Phoibos 150 NAP) equipped with a CEM 9 channeltron detector and a 300 μm entrance aperture to the first differential pumping stage. The analyzer entrance normal was oriented 70° from the incident X-ray beam and 20° from the surface normal of the sample.

GaP(110) single crystals (Princeton Scientific) were cleaned in vacuum using a series of sputter–annealing cycles, using methods described in the literature.²⁰ Each cycle consisted of 1 kV Ar⁺ ion bombardment followed by sample heating to 500–550 °C. The cycles were repeated until no C 1s signal was detected. After similar treatments of GaP(110) in a separate chamber, a 1 × 1 LEED pattern was observed. The base pressure of the chamber was 3–4 × 10⁻¹⁰ Torr. We checked for radiation- and photoelectron-induced chemistry by (1) monitoring spectra over time, (2) monitoring spectra and changing the position sampled on the crystal, and (3) monitoring spectra and increasing the background pressure. No differences in the spectra induced by these changes were observed. The spectra in this article were signal-averaged over several scans, and the times to acquire the scans were 144 s (Ga 3d), 40 s (P 2p), and 360 s (O 1s). When photon energies were changed, the binding energies were calibrated using the Ga 3d peak, which originates from high kinetic energy photoelectrons and thus probes deeply into the substrate. All binding energies
2.2. Density Functional Theory. We performed DFT calculations with periodic boundary conditions to identify relevant water configurations on the GaP(110) surface and assess their associated thermodynamic stabilities. All calculations were performed using the software package VASP, the PBE exchange-correlation functional, and default projector augmented wave (PAW) potentials to describe nuclei and frozen core electrons (1s2s2p3s3p3d for Ga, 1s2s2p for P, and 1s for O). We described the rest of the electrons using a planewave basis with a kinetic energy cutoff of 800 eV. We used $6 \times 4 \times 1$ k-point sampling based on the Monkhorst-Pack scheme. The Brillouin zone was integrated using the Gaussian smearing method with smearing width equal to 0.05 eV. For the calculation of an isolated water molecule, we only sampled the $\Gamma$ point with a smearing width equal to 0.001 eV. Overall, with these computational parameters, the total energy was converged to within 1 meV/atom.

We used the same model for the GaP surface as that used in previous work by our group (a seven-layer slab generated from a $1 \times 2$ unit cell of the GaP(110) surface, resulting in four GaP formula units in each layer). We modeled different water coverages, defined as the number of adsorbate molecules divided by the number of Ga adsorption sites per surface, ranging from 0.25 to 2 monolayers (ML). Adsorbates were divided by the number of Ga adsorption sites per surface, because at room temperature gaseous (liquid) water is unstable (stable) in the reservoir. More information regarding the use of the water chemical potential in constructing the phase diagram can be found in previous work in which a similar diagram was computed for a different surface. We calculated the adsorption free energy, $\Delta \Omega$, dependent on the water chemical potential, $\mu_w$, using the following equation:

$$\Delta \Omega(T, p) = \frac{1}{2} (G_{\text{slab}+nW} - G_{\text{slab}} - n \mu_w(T, p))$$

$G_{\text{slab}+nW}$ is the free energy of the GaP slab-water complex containing $n$ water molecules, and $G_{\text{slab}}$ is the free energy of the bare GaP slab. Both energies include zero point energy and thermal corrections at room temperature. $n$ is the total number of water molecules adsorbed on both sides of the slab. $\mu_w$ is the

<table>
<thead>
<tr>
<th>Coverage</th>
<th>Configurations</th>
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<tr>
<td>0.25 ML</td>
<td>0% D 100% D</td>
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<tr>
<td>0.5 ML</td>
<td>0% D 50% D</td>
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<td>0.75 ML</td>
<td>0% D 33% D</td>
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<td>1 ML</td>
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<tr>
<td>2 ML</td>
<td>0% D 50% D</td>
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Each water configuration is defined by the coverage (expressed in ML) and the degree of dissociation (D).

are referenced to $E_b = 0$ eV binding energy. Spectra were fit to Gaussian–Lorentzian convolutions, and the full width at half-maximum of each peak was fixed for a given spectrum. The integrated intensities of the spin–orbit split peaks of the P 2p level were fixed by the required 2:1 peak-area ratio.
chemical potential of water, which depends on temperature, $T$, and pressure, $p$. We introduce the factor $1/2$ because as discussed above we model adsorbates on both sides of the slab, but we are interested in the adsorption properties of one surface only. The chemical potential $\mu_w$ is shifted from water-poor to water-rich conditions using the parameter $\Delta \mu_w$, as illustrated in the following equation:

$$\mu_w = \Delta \mu_w + G_w^{\text{gas}}$$

$G_w^{\text{gas}}$ is the free energy of a water molecule in the gas phase and includes zero point energy and thermal corrections at room temperature. When $\Delta \mu_w$ is equal to 0 eV, $\mu_w$ is the chemical potential of water in the gas phase, which corresponds to water-rich conditions at the surface; when $\Delta \mu_w$ is equal to $-0.09$ eV, $\mu_w$ is the chemical potential of water in the liquid phase describing water-poor conditions at the surface. The value $-0.09$ eV is the difference between the experimental values of the water chemical potential in the liquid and gas phases at room temperature.

3. RESULTS AND DISCUSSION

3.1. Ambient Pressure Photoelectron Spectroscopy: Isothermal Conditions. X-ray photoelectron spectroscopy can be used to probe the chemical states of surface-bound species because changes in the binding energies of core-level electrons are sensitive to both the formal oxidation state and local chemical environment of the probed atom. The probing depth of the measured spectrum is defined by the inelastic mean free path of the ejected photoelectrons, and we used photon energies lower than those available in conventional laboratory X-ray sources to increase the surface sensitivity of our measurements.

Figure 1a shows O 1s core-level spectra from GaP(110) after exposures to $H_2O$ in UHV and in situ for up to $1 \times 10^{-7}$ Torr to 0.9 Torr $H_2O$: (a) O 1s spectra and (b) normalized Ga 3d spectra. Figures on the left show data acquired at $4 \times 10^{-9}$ Torr base pressure after exposing the sample to $H_2O$ at $1 \times 10^{-7}$ Torr. Figures on the right show in situ measurements at the indicated pressures. Bold lines are experimental data, and fine lines are fitted component contributions.

Figure 1. Isothermal APPES spectra from GaP(110) after exposures to $H_2O$ in UHV and in situ for up to $1 \times 10^{-7}$ Torr to 0.9 Torr $H_2O$: (a) O 1s spectra and (b) normalized Ga 3d spectra. Figures on the left show data acquired at $4 \times 10^{-9}$ Torr base pressure after exposing the sample to $H_2O$ at $1 \times 10^{-7}$ Torr. Figures on the right show in situ measurements at the indicated pressures. Bold lines are experimental data, and fine lines are fitted component contributions.
observed. This peak is attributed to photoelectrons originating from vapor phase H$_2$O. At 0.4 Torr, a fourth peak at 533.7 eV, labeled *, was observed that we attribute to photoelectrons originating from interacting coadsorbed OH and H$_2$O species. Above 0.1 Torr, the total signal intensity decreases because of photoelectron scattering away from the analyzer aperture.

The assignments of OH and H$_2$O to the peaks at 531.6 and 532.7 eV, respectively, are based on literature assignments: the adsorption of H$_2$O and OH has been studied on a number of surfaces, including metals,31,33 oxides,32,34 and semiconductors.35 Zhang and Ptasinska recently studied the interactions of water with GaAs(100)35 and GaP(111)36 by high-pressure XPS. These papers assign four separate peaks associated with both O and OH bonded to surface Ga, which is based on methods in a prior study of GaAs(100).37 Herein, after consideration of available evidence and the limitations of the resolution of these particular measurements, we assign only OH and H$_2$O peaks (use of additional peaks was not found to improve the overall fit in a statistically significant result).

Figure 1b shows Ga 3d spectra excited by 300 eV photons in both the low-coverage UHV regime described above and in situ in the presence of an elevated pressure of H$_2$O in the background. The substrate Ga 3d peak, in which the two spin−orbit split components are unresolved, is located at 19.5 eV. At and above a pressure of 1 × 10$^{-7}$ Torr, a new peak at higher binding energy (ΔE = 1.1 eV) was observed. This peak grows with increasing H$_2$O pressure up to 0.4 Torr. The energy of this peak relative to that for GaP is consistent with formation of a Ga−OH species. The presence of this species was not observable in Ga 3d spectra for the low-coverage regime within a level of high statistical significance for our fitting. This is due in part to contributions from subsurface Ga to the signal, the fact that not every surface Ga interacts with OH (see below), and that there is in general a very small chemical shift associated with the formation of Ga−OH.

Figure 2a shows P 2p spectra taken on GaP(110) under the same conditions as above. For the clean GaP(110) surface, the P 2p region shows a partially resolved set of peaks from the 2p$_{1/2}$ and 2p$_{3/2}$ spin−orbit split components at 129.8 and 128.9 eV, respectively. The two peak contributions were strictly fit according to the required 2:1 area ratio of these peaks. For exposures up to 6 langmuirs H$_2$O, no changes in the P 2p spectra were observed. Above this exposure and at higher background H$_2$O pressures (above UHV), the spectra do change and it is necessary to include a new P 2p doublet at binding energy slightly higher than that of the substrate in order to fit the spectra. The peaks are detected with small signal intensity in UHV after exposure to water, and their intensities increase considerably when the surface is probed in situ at higher pressures (up to 0.4 Torr). An expanded view of these new peaks is shown in Figure 2b, which directly compares the GaP(110) surface when clean and in the presence of 0.4 Torr H$_2$O. After the pressure was raised to 0.9 Torr for approximately 5 min and then decreased by a factor of 9, the P 2p spectrum associated with the high-pressure condition remained, which shows that an irreversible reaction had taken place.

The data in Figure 2 indicate the presence of a new phosphorus chemical state with a P 2p binding energy slightly greater than that of the Ga-bound P of the GaP(110) substrate. We assign the two new H$_2$O pressure-induced spin−orbit-split peaks at 129.9 and 130.8 eV to surface P−H species. Previous work on H$_2$S dissociation on InP clearly shows that the presence of P−H on the surface of a phosphide semiconductor is associated with P 2p peaks located at binding energies only slightly higher than those of the substrate. This is consistent with the charge transfer (0.7 e) from surface P predicted to accompany formation of the negatively charged hydride.15
The P−H and Ga−OH component peak areas increased as the H2O pressure was increased because in these conditions pressure is proportional to surface coverage. The Hertz−Knudsen equation describes the relationship between the flux of gas to the surface, Z, and the pressure, P: \( Z = N P (2 \pi M R T)^{-1/2} \), where \( T \) is the temperature and \( M \) is the molar mass of the gas. The surface coverage, \( \theta \), is equal to the product of the flux and the residence time, \( \tau: \theta = Z \tau \). The rate of dissociation is given by \( R_{\text{diss}} = k_{\text{diss}} \theta \); therefore, at low coverages, the rate of dissociation increases with increasing H2O pressure.

There is a related mechanism that has been discussed in the literature that may further explain the origins of our observed increase in concentration of Ga−OH and P−H at high H2O pressures. Andersson et al.\(^3\) reported dissociation of H2O on Cu(110) that is driven by stabilization of adsorbates through H2O(donor)−OH(acceptor) complexes. The increased coverage of H2O on the surface that is associated with increased background pressure (see above) leads to a greater degree of hydrogen bonding among adsorbed H2O and OH. The H2O−OH bond is stronger than the H2O−H2O bond.\(^3\) Through Brønsted−Evans−Polanyi relations for water dissociation,\(^3\) a lower activation barrier for water dissociation results.\(^3\) This analysis from the literature provides a mechanism by which increased H2O pressure and therefore H2O coverage can result in an increase in amount of stable dissociation products.

The experimental evidence presented in Figures 1 and 2 indicates that the interaction with H2O induces the formation of surface P−H, Ga−OH, and molecular H2O on GaP(110). These results are consistent with a number of observations of spontaneous H2O dissociation on related surfaces in recent years: GaAs(100),\(^1\) GaP(111),\(^3\) GaAs nanowires,\(^4\) InP(100),\(^3\) and GaN(1011),\(^4\) as well as several recent theoretical studies on related III−V surfaces.\(^5\) We next performed periodic slab calculations using DFT to verify the thermodynamic stabilities of these species under experimental conditions.

### 3.2. Adsorbate−Surface Phase Diagram from Density Functional Theory

Our DFT results, presented below, are in very good agreement with the experimental observations: at room temperature and in water-poor conditions, Ga−OH, adsorbed molecular H2O, and P−H species are found to be thermodynamically stable on the GaP(110) surface. The stability of these species is shown by the computed H2O phase diagram on GaP(110) (Figure 3), which illustrates the thermodynamic stabilities of several water configurations for different water conditions at the surface.

In order to build the phase diagram, we modeled several possible initial configurations of water, varying coverage and degree of dissociation. Coverages considered range from 0.25 ML (i.e., one water molecule per surface unit cell) to 2 ML (i.e., eight water molecules per surface unit cell), where coverage is defined as the number of adsorbate water molecules divided by the number of Ga adsorption sites per surface unit cell. For each coverage, we investigated an undissociated configuration and a dissociated configuration. Table 1 displays the configurations considered for each coverage along with its respective degree of dissociation. At 0.25 ML, the one water molecule in the unit cell is dissociated heterolytically by adsorbing the hydroxide on a surface Ga atom and the proton on a neighboring surface P atom. In this way, 100% dissociation is obtained. At 0.5 ML, two water molecules are in the unit cell. We investigated the effect of dissociating one molecule, which corresponds to 50% dissociation, and then also adding an undissociated water molecule to this configuration, reaching 0.75 ML coverage with 33% dissociation. These three configurations were investigated to study whether coadsorbed water molecules assist dissociation. Finally, we modeled 1 and 2 ML coverages, both with 50% dissociation within the first monolayer. These two configurations were considered in order to investigate the effect of a solvating layer (i.e., the second water monolayer) on dissociation occurring in the first monolayer. Note that the dissociated configurations considered in this work have different geometries with respect to those modeled in previous work.\(^1\)

In the phase diagram, for each value of water chemical potential (i.e., water conditions at the surface), the configuration with the most negative adsorption free energy represents the most thermodynamically stable one. Overall, the 1 ML, half-dissociated configuration (blue dashed line in Figure 3) represents the most stable water configuration for both water-poor and water-rich conditions. This configuration involves the Ga−OH, P−H, and adsorbed molecular H2O species observed in this work by APPES. In addition, this half-dissociated configuration, Ga−OH and H2O species interact via hydrogen bonding (Figure 4), which was also observed here experimentally (peak labeled * in Figure 1a).

In addition to the agreement between experimental and computational findings, the phase diagram yields three other important results. First, we observe that adsorption of water is always favored except for the 2 ML undissociated configuration and the 0.25 ML dissociated configuration when approaching water-poor conditions. In fact, only under these conditions do the lines corresponding to these configurations fall above the black horizontal line (0 ML) representing the clean surface (i.e., the adsorption free energy becomes positive and adsorption of water in these configurations is no longer thermodynamically favored). Second, inspection of the water phase diagram reveals that for coverages larger than 0.25 ML, water dissociation is always thermodynamically favored even in water-poor conditions. In fact, each dissociated configuration (dashed lines) is...
more stable (lower free energy) than the corresponding undissociated configuration (solid lines), except for the 0.25 ML case. In previous work, water dissociation was predicted to be favored only for coverages larger than 2 ML. Here we find water dissociation to be favorable at much lower coverages (0.5 ML), resulting from finding a more stable adsorption geometry for the partially dissociated configurations than was found earlier. In particular, in our current structures, an adsorbed hydroxide deriving from water dissociation is stabilized by the presence of a coadsorbed, undissociated water molecule that promotes dissociation via hydrogen-bonding, as shown in Figure 4. The 0.25 ML anomaly is therefore easy to understand: dissociation is not favored at that low coverage because there are not enough water molecules on the surface to promote dissociation via hydrogen bonding. Third, relative adsorption free energy values of the 2 ML 50% D and 1 ML 50% D configurations suggest that at room temperature the formation of a solvation layer on top of the first adsorbed layer of water is not thermodynamically favored (i.e., the 2 ML 50% D configuration is higher in energy than the 1 ML 50% D configuration). This occurs because hydrogen bonds among the first and second monolayers are not strong enough to overcome the entropic contribution that drives the evaporation of the second monolayer at room temperature. In addition, this finding is consistent with the results of molecular dynamics simulations of liquid water in contact with metal surfaces reported by Limmer et al., which shows the formation of a hydrophobic water layer on the surface.

In summary, our computational findings are in excellent agreement with experimental results: we predict that all the experimentally observed species are thermodynamically stable at room temperature and in water-poor conditions. In addition, we find that water adsorption and dissociation is always thermodynamically favored on this surface if the Ga–OH species are stabilized by a hydrogen bond with an undissociated H2O molecule, with 1 ML being the most thermodynamically favored coverage under water-poor conditions.

3.3. Ambient Pressure Photoelectron Spectroscopy: Isobaric Conditions. Additional experiments were conducted to assess the thermal stabilities of these adsorbates as well as to study the oxidation of GaP(110) caused by the presence of H2O. Figure 5 shows isobaric APPES measurements of O 1s, P 2p, and Ga 3d spectra taken in situ at 0.1 Torr H2O from 38 to 360 °C. O 1s spectra (Figure 5a) indicate that increasing the sample temperature in the presence of 0.1 Torr H2O causes the growth of a surface oxide phase that is characterized by an O 1s peak at 530.4 eV. When the sample is heated, evidence for this new oxide peak appears already at 80 °C, which was the lowest elevated temperature examined.

The peaks corresponding to surface-bound OH and H2O remain at all elevated temperatures examined. The presence of molecular H2O adsorbed on the surface at such high temperatures seems remarkable; however, it is consistent with results from prior high-pressure photoelectron spectroscopy studies in the literature. Surface-bound molecular H2O at elevated temperatures in high H2O pressures has been reported previously on the surface of TiO2(110). In 0.375 Torr H2O, surface-bound molecular H2O was observed on GaP(111) up to 400 °C.

P 2p spectra recorded at 0.1 Torr H2O (Figure 5b) indicate the presence at elevated temperatures of a new peak at higher binding energy ($\Delta E = 4.7$ eV) than that of P in GaP(110). The intensity of this peak (also due to a partially resolved spin–orbit split doublet) increases with increasing temperature up to the highest temperature examined, 360 °C. The high binding energy of this peak is indicative of oxidation of surface P. An oxide peak at 21.3 eV appears and increases in intensity in the Ga 3d spectra at elevated temperatures (Figure 5c). This oxide peak is 0.8 eV higher in binding energy than that of the surface OH identified in the isothermal measurements (at 20.6 eV; Figure 1b).

On the basis of the measured core-level shifts, we can put forward some description of the surface oxide using the available literature. We observe the difference in P 2p peaks between the surface oxide and GaP to be $\Delta E = 4.7$ eV. Prior work on the oxidation of GaP reports that this shift for GaPO4 is 5.5 eV and for P2O5 is 5.8 eV. However, studies of P 2p core-level shifts associated with the oxidation of InP report an average of 4.7 eV for InPO4 and 6.6 eV for P2O5. The binding energy associated with a phosphine oxide is about 2 eV lower than that observed here. These comparisons suggest to us that the charge on oxidized surface P in our study is similar to that in GaPO4, although the structure of the oxide itself is likely unique to the surface. Given the coinciding observation of both Ga oxide and P oxide species, we currently favor assignment of a network structure that may contain bridging oxygen atoms between Ga and P, as has been suggested in recent studies of water adsorption on GaAs(100) and GaP(111), although we do not suggest a specific structure here. The oxides observed here at high temperature are unlikely to play an important role in the chemistry that motivates this report, because electrochemical CO2 reduction experiments take place at room temperature and under cathodic polarization. It has been observed in these conditions that metal oxide electrodes are reduced to metals. We can expect similar behavior for GaP.

The thermal stability of the P–H species identified in Figure 2 can also be assessed using the isobaric P 2p measurements in Figure 5b. The areas of the peaks at 129.9 and 130.8 eV decrease with increasing temperature, up to 360 °C. At this temperature, the hydride peaks’ areas are decreased by 90%. The implications of this thermal stability for solar fuel reactions will be discussed below.

3.4. Role of Negatively Charged Hydrides in H+ and CO2 Reduction Reactions. Our experimental and theoretical results provide insights that aid discussions aimed broadly at the role of negatively charged surface hydride species in solar-driven photoelectrochemical and photocatalytic CO2 reduction reactions. Without molecular catalysts, illuminated
GaP photocathodes under applied cathodic potential in aqueous CO₂ solutions reduce CO₂ to products including HCOO⁻, HCOOH, CH₃OH, and HCOH.51–54 Alternate product distributions, including significant yields of CO, are observed in nonaqueous electrolytes.55 It is known that the addition of a small amount of water into organic solvents accelerates the hydrogenation of CO₂ and therefore the formation of HCOO⁻/HCOOH. In this way, H₂O is known to play an important role in the reaction by serving as a proton source.56

More specific observations concerning hydrogen can be made in the context of proton-coupled electron transfer. The carbon atom of the amphoteric CO₂ molecule is susceptible to attack by nucleophilic negatively charged surface hydrides.57 This activation induces a negative charge on the oxygen atoms, which can be stabilized by a Brønsted acid.57 Although the role of the GaP surface in aqueous CO₂ reduction reactions is not understood, some mechanistic reports are available for GaAs electrodes, and the reported conclusions are likely to be at least in essence applicable to GaP. Frese and Canfield58 studied pH-dependent GaAs electrochemistry and concluded that the rate of CO₂ reduction to methanol is limited by a surface chemical reaction involving adsorbed H (Hₚₚ) and unknown surface intermediates. Possible intermediates include adsorbed CO, COH, CH−OH, CH₂−OH, and O−CH₃. These observations highlight the important roles that Hₚₚ species play in both the initial activation of CO₂ molecules and additional hydrogenation steps to hydrocarbons and alcohols.

The Hₚₚ species has also been proposed to be intimately involved in Py-catalyzed CO₂ reduction, which was the primary motivation for this study. Keith and Carter showed that one possible source of the experimentally observed reduction wave associated with CO₂ reduction in aqueous Py/PyH⁺ is the two-electron reduction of Py to ortho- or para-dihydropyridine (o- and p-DHP), Py + 2H⁺ + 2e⁻ → DHP.14 This suggestion is relevant to our observation of negatively charged Hₚₚ in water environments: one possible formation mechanism for surface-bound DHP is hydride transfer to Py, which is bound to the surface via the N lone pair, followed by or concomitant with proton transfer from a Brønsted acid in solution.15,17 We show here that the interaction of water with GaP(110) yields a concentration of Hₚₚ that could facilitate such a reduction of surface-bound catalysts.

Other proposed mechanisms explicitly emphasize the importance of Hₚₚ for Py-catalyzed CO₂ reduction, and our work may also inform these analyses. In a related theoretical study, the authors investigated the interaction of water with GaP(110) and observed the formation of Hₚₚ, which could play a role in the catalytic process.18

Figure 5. Isobaric APPES measurements on GaP(110) in situ at 0.1 Torr H₂O from 38 to 360 °C: (a) O 1s spectra, (b) normalized P 2p spectra, and (c) normalized Ga 3d spectra. Bold lines are experimental data, and fine lines are fitted component contributions.
study of Pt electrochemistry, Batista and co-workers\textsuperscript{42} suggested an acid-catalyzed reduction mechanism, in which the electrochemical reduction of \( \text{PyH}^+ \) yields a surface-bound hydrogen, \( \text{Pt} - \text{H}_{\text{ads}} \), that facilitates \( \text{CO}_2 \) reduction by proton-coupled hydride transfer, \( \text{CO}_2 + \text{Pt} - \text{H}_{\text{ads}} + \text{PyH}^+ + e^- \rightarrow \text{Py} + \text{Pt} + \text{HCO}_2\text{H} \). A recent experimental investigation of this system by Lebegue et al.\textsuperscript{7} provides further evidence that the initial mechanistic role of \( \text{PyH}^+ \) is to establish a concentration of \( \text{H}_{\text{ads}} \). This study used Ir, Pt, Au, and glassy carbon electrodes, materials with differing metal–hydrogen bond strengths, to assess the role of reduction of \( \text{PyH}^+ \) to \( \text{Pt} + \text{H}_{\text{ads}} \) in catalysis of \( \text{CO}_2 \) reduction. It was found that only Pt and Ir facilitate the formation of \( \text{H}_{\text{ads}} \) and subsequently produce a catalytic interaction between \( \text{CO}_2 \) and \( \text{H}_{\text{ads}} \). These studies have provided convincing evidence that the first mechanistic step of Py-catalyzed \( \text{CO}_2 \) electroreduction on Pt, and the origin of the observed cathodic wave at \( -0.6 \) V in cyclic voltammetry studies, is the one-electron reduction of \( \text{PyH}^+ \) to \( \text{H}_{\text{ads}} \). In this study, we do not consider the molecular cocatalyst, but this proposed mechanism from the literature is topical because it also emphasizes the importance of the \( \text{H}_{\text{ads}} \) species.

The efficiency and selectivity of catalyzed \( \text{CO}_2 \) reduction processes may therefore be related to the nature of the negatively charged hydride on electrode surfaces. As indicated in ref \textsuperscript{7}, materials with intermediate free energies of \( \text{H} \) adsorption (Pt and Ir), which are also materials with a low overpotential for the hydrogen evolution reaction (HER),\textsuperscript{59} produce a catalytic interaction between \( \text{PyH}^+ \) and \( \text{CO}_2 \). Keith and Carter\textsuperscript{15} noted that materials with low HER overpotential should be active for \( \text{CO}_2 \) reduction because they should also facilitate hydrogen transfer to \( \text{CO}_2 \). GaP however is a high HER selectivity toward methanol observed for Py-catalyzed \( \text{CO}_2 \) overpotential material. In order to understand the high selectivity for methanol observed for Py-catalyzed \( \text{CO}_2 \) reduction on GaP, it is useful then to consider the strength of the \( \text{P} = \text{H}_{\text{ads}} \) interaction, of which we provide an experimental measure in this study, in the context of electrochemical HER.

When limited by the Tafel reaction, \( 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \), the most important descriptor for HER activity is the binding free energy of \( \text{H} \).\textsuperscript{59} For metal electrodes, the relationship between HER exchange current density and free energy of \( \text{H} \) adsorption follows the Sabatier principle. Materials with intermediate \( \text{H} \) adsorption free energies, such as Pd, Pt, and Ir, exhibit the highest HER activities. The temperature at which \( \text{H} \) desorbs from surfaces should serve as a rough experimental indicator of the strength of metal–\( \text{H} \) bonds (rough because the energy associated with the desorption temperature overestimates the metal–\( \text{H} \) bond strength if there is an activation barrier for \( \text{H} \) dissociation). When a sample is heated in vacuum, the rate-limiting step for \( \text{H}_2 \) desorption is typically the surface recombination reaction, \( 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \). For example, on Ag(111), a poor HER catalyst that is associated with a low free energy of \( \text{H} \) adsorption, a saturation coverage of atomic hydrogen leads to \( \text{H}_2 \) desorption at about \(-73^\circ\text{C}\)\textsuperscript{60} (again, a value that includes the added thermal energy required to overcome the \( \text{H}_2 \) dissociation activation barrier). The desorption peak for Pt(111), a good HER catalyst that is associated with an intermediate free energy of \( \text{H} \) adsorption, occurs below \( 130^\circ\text{C} \).\textsuperscript{51} For W surfaces, which are poor HER catalysts and associated with large free energies of \( \text{H} \) adsorption, \( \text{H}_2 \) desorption occurs at higher temperatures of 130 to 230 \( ^\circ\text{C} \).\textsuperscript{62} In this context, the experimentally observed thermal stability for \( \text{P} = \text{H}_{\text{ads}} \) on GaP(110) is very large, given that this species is observable at an electrode temperature of 360 \( ^\circ\text{C} \) in 0.1 Torr \( \text{H}_2\text{O} \).

Although the desorption temperature is an imperfect descriptor for activity, the measured thermal stability of the \( \text{P} = \text{H}_{\text{ads}} \) species on GaP(110) is consistent with its associated high HER overpotential. The inability of GaP to catalyze \( \text{H}^+ \) reduction is likely an important factor influencing the near-100% faradaic efficiency for methanol generation from Py-catalyzed \( \text{CO}_2 \) electroreduction using GaP. It has been observed in the literature that glassy carbon, which is also a poor HER catalyst, does not produce any cathodic current associated with \( \text{CO}_2 \) reduction in similar conditions.\textsuperscript{63} However, there is a very important distinction in this case: glassy carbon is a poor HER catalyst because of its contrasting extremely weak interaction with \( \text{H} \).

The following observations in the literature further support the claim that the \( \text{CO}_2 \) reduction selectivity of GaP relates to its inability to catalyze electrochemical HER. Because GaP is not catalytically active for HER in water, a portion of photoexcited electrons transported to the GaP—electrolyte interface participate instead in competing electrode decomposition reactions.\textsuperscript{64} In acidic conditions, therefore, GaP is not photoelectrochemically stable for HER. No activity is reported after 15 h in ref 65. In stark contrast, when photoexcited electrons in GaP drive the reduction of \( \text{CO}_2 \) in aqueous Py/PyH\textsuperscript{+}, the electrode is stable for at least 30 h.\textsuperscript{7} Although both reactions are believed to require the participation of \( \text{H}_{\text{ads}} \) their associated electrochemical stabilities differ considerably. This contrast could originate from the fact that the execution of the electrochemical Tafel reaction, \( 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \), requires \( \text{H}_{\text{ads}} \) diffusion, whereas acid-catalyzed \( \text{CO}_2 \) reduction or Py reduction to \( \text{DHP} \) requires no surface diffusion.\textsuperscript{64} When participating in acid-catalyzed \( \text{CO}_2 \) reduction reactions in the presence of Py/PyH\textsuperscript{+}, photoexcited electrons in GaP could be efficiently shuttled to the catalyst or \( \text{CO}_2 \) which prevents their involvement in competing electrochemical decomposition reactions.

4. CONCLUSIONS

We have presented an experimental and theoretical investigation of the interaction of water with GaP(110). Experimentally we determine that exposure to water produces a partially dissociated surface layer consisting of \( \text{Ga} = 
\text{OH} \), \( \text{molecular} \: \text{H}_2\text{O} \), and \( \text{P} = \text{H} \) species. The coverages of \( \text{Ga} = \text{OH} \) and \( \text{P} = \text{H} \) increase with increasing \( \text{H}_2\text{O} \) pressure up to the largest pressure studied, 0.4 Torr. Periodic DFT calculations were used to identify relevant water configurations on the GaP(110) surface and calculate their ambient thermodynamic stabilities. The calculations confirm the thermodynamic stability of the partially dissociated layer identified experimentally. Isobaric measurements at 0.1 Torr \( \text{H}_2\text{O} \) pressure were used to probe the thermal stabilities of adsorbed species as well as the oxidation of surface Ga and P. \( \text{P} = \text{H} \) was observed on the surface up to 360 \( ^\circ\text{C} \), which indicates a relatively high thermal stability for this species. Both surface Ga and P oxidize during temperature elevation in the presence of water vapor, beginning between 80 and 120 \( ^\circ\text{C} \).

These observations enable us to discuss the role of negatively charged hydrides in photoelectrocatalytic \( \text{H}^+ \) and \( \text{CO}_2 \) reduction reactions and to further interpret related results from the literature. We hypothesize that the observed stability of \( \text{P} = \text{H} \) species contributes to the high faradaic efficiency for methanol generation associated with illuminated GaP in...
aqueous solutions of CO₂ and Py/PyH⁺. The strongly bound surface hydrides lead to low activity for the hydrogen evolution reaction, which directly competes with CO₂ reduction under the reported conditions.

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Notes
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