

Ultrafast Electron Dynamics at the Water-Modified InP(100) Surface

Jonathan Diederich, Agnieszka Paszuk, Isaac Azahel Ruiz Alvarado, Marvin Krenz, Mohammad Amin Zare Pour, Diwakar Suresh Babu, Jennifer Velazquez Rojas, Christian Höhn, Yuying Gao, Klaus Schwarzburg, David Ostheimer, Rainer Eichberger, Wolf Gero Schmidt, Thomas Hannappel, Roel van de Krol, and Dennis Friedrich*

The interaction of water molecules with semiconductor surfaces is relevant to various optoelectronic phenomena and physicochemical processes. Despite advances in fundamental understanding of water-exposed surfaces, the detailed time- and energy-resolved behavior of excited electrons remains largely unexplored. Here, the effects of water exposure on the near-surface electron dynamics of phosphorus-terminated $p(2\times 2)/c(4\times 2)$ -reconstructed indium phosphide (100) (P-rich InP) are studied experimentally and matched to theoretical calculations. The P-rich InP surface, consisting of H-passivated P-dimers, serves as a model for other P-containing III-V semiconductors such as gallium phosphide (GaP) or aluminum indium phosphide (AlInP). Electron dynamics near the surface are probed with femtosecond resolution using time-resolved two-photon photoemission (tr-2PPE), a pump-probe spectroscopic technique. Pulsed water exposure preserves electronic states and significantly increases lifetimes at the conduction band minimum (CBM). Density-functional theory (DFT) calculations attribute these findings to suppression of surface vibrational modes in the top P-layer by water exposure, reducing electronic transition probabilities of near-band-gap surface states. The results suggest that many near-surface state lifetimes reported in ultra-high vacuum may change significantly upon electrolyte exposure. These states may thus contribute more strongly to surface reactions than traditionally assumed. Demonstrating this effect for the technologically relevant P-rich InP surface opens new opportunities in this underexplored area of surface electrochemistry.

1. Introduction

Renewable hydrogen production is a key factor in the transition toward a sustainable energy future. Among the various methods for solar hydrogen generation, photoelectrochemical (PEC) cells offer a promising alternative to the conventional photovoltaic-electrolyzer systems. Notably, the highest solar-to-hydrogen efficiencies to date have been reported in systems based on III-V semiconductor materials^[1,2] due to their direct band gaps, high electron mobilities, low exciton binding energies, and high degree of band gap tunability.

In this context, indium phosphide (InP) emerges as a significant material, in part due to its use as a reference material for various III-V semiconductors such as aluminum indium phosphide (AlInP), gallium phosphide (GaP), or gallium indium phosphide (GaInP), but also as an established semiconductor in PEC^[3–5] and photovoltaic (PV)^[2] applications of its own. Its outstanding optoelectronic properties, including a direct band gap of 1.34 eV and high

J. Diederich^[+], D. S. Babu, J. Velazquez Rojas, C. Höhn, Y. Gao, K. Schwarzburg, R. Eichberger, R. van de Krol, D. Friedrich
Institute for Solar Fuels
Helmholtz-Zentrum Berlin für Materialien und Energie GmbH
14109 Berlin, Germany
E-mail: friedrich@helmholtz-berlin.de



The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/admi.202500463>

[+]Present address: Frick Chemistry Laboratory, Princeton University, Princeton, NJ 08544, USA

© 2025 The Author(s). Advanced Materials Interfaces published by Wiley-VCH GmbH. This is an open access article under the terms of the [Creative Commons Attribution](#) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/admi.202500463

J. Diederich^[+], D. S. Babu, J. Velazquez Rojas, R. van de Krol
Institut für Chemie
Technische Universität Berlin
10623 Berlin, Germany

A. Paszuk, M. A. Zare Pour, D. Ostheimer, R. Eichberger, T. Hannappel
Fundamentals of Energy Materials
Institute of Physics
Technische Universität Ilmenau
98693 Ilmenau, Germany

A. Paszuk, M. A. Zare Pour
BMFTR Junior Research Group PARASOL
Institute of Physics
Technische Universität Ilmenau
98693 Ilmenau, Germany

I. A. Ruiz Alvarado, M. Krenz, W. G. Schmidt
Lehrstuhl für Theoretische Materialphysik
Universität Paderborn
33095 Paderborn, Germany

electron mobility,^[6] also make InP(100) a key material for optoelectronic applications such as photonic integrated circuits.^[7–9] The phosphorus-terminated (P-rich) InP surface is a general motif for many related III-V surfaces, such as GaP, GaInP, or Al-InP. Such surfaces are terminated by P-P dimers passivated by one H atom (P-P-H), and due to the use cases of these materials highly relevant for PEC, optoelectronics, etc.^[10–13] The current efficiency record for voltage-assisted PEC water splitting uses an InP photoabsorber,^[2–4,14–16] while the record unassisted PEC water splitting cells have an InP-based III-V heterostructure stack with an AlInP window layer.^[1] Two well-defined and highly reproducible surface reconstructions of InP – the P-rich $p(2\times 2)/c(4\times 2)$ -reconstructed and the In-rich $(2\times 4)(100)$ surfaces – are known and described in detail, each with its own electronic energy levels, surface states, dynamics therein, as well as surface passivation and stability that affect its overall performance.^[10,17–19]

The natural surface properties of III-V semiconductors often experience significant modifications in the aqueous environments found in PEC cells.^[11,17,18,20–22] Heller et al. demonstrated p-doped InP (p-InP) to be more stable than other III-V semiconductors, retaining functionality for over a week under realistic PEC conditions with a thin surface oxide layer, before non-surface-related issues led to failure.^[23] In 1982, Aharon-Shalom et al. explored the direct deposition of catalysts onto etched p-InP layers, observing metal oxide formation at the interface, which required periodic anodization for oxide regrowth to maintain stability under PEC conditions.^[16] The effects of these naturally formed oxide layers on the near-surface electron dynamics have not been explored in detail to date. The requirement for anodization of surface oxides can be avoided by depositing metal oxide protection layers before PEC operation; such layers tend to be more electrochemically stable under operando conditions than the In- and P-oxides that form naturally at the surface.^[15,24–28] In addition to protecting the bulk of the semiconductor, these layers should also transport charge carriers from the semiconductor surface to the electrolyte, and are crucial in separating majority and minority charge carriers, thereby, with an appropriate heterointerface, acting as selective contacts and reducing recombination. Because of this, despite the additional internal interfaces introduced, non-native metal oxide protection/passivation layers tend to improve PEC performance and stability.^[15,25,26,29–31] The effects of environmental exposure of InP to water, as well as the resulting, e.g., phosphate formation and other processes are not well understood, and may impact device behavior significantly, especially for biomedical sensors and other technologies exposed to non-sterile, non-dry environments.^[11,16] Thus, understanding the details of surface structures and charge carrier transport processes under aqueous conditions is critical for designing effective surfaces for optoelectronics and PEC cells.

The present research is based on a previous study, in which we investigated the P-rich, $p(2\times 2)/c(4\times 2)$ -reconstructed, InP

(100) surface, prepared by metalorganic vapor phase epitaxy (MOVPE).^[32] Using time-resolved two-photon photoemission (tr-2PPE), we identified nine electronic states in the near-surface region and tracked photoinduced electron dynamics. In a subsequent study on this surface, we had used the distinct surface states on P-rich InP as a sensitive probe for understanding modifications to near-surface ultrafast electron dynamics caused by the step-wise deposition of TiO_2 using atomic layer deposition (ALD).^[33,34] Charge carrier lifetimes in surface conduction band states on the bare P-rich InP were short, less than 2 ps for the lowest-energy conduction band state, significantly below the timeframes generally associated with surface reaction kinetics.^[35] There is still a research gap in understanding how these surface states are influenced by water molecules adsorbed on the surface, which commonly occurs under operating conditions in PEC cells.

In the present work, we aim to gain understanding of the changes in the near-surface state dynamics of the InP surface upon exposure to water. While not the same as full immersion in a liquid electrolyte, water exposure can lead to both physisorption and chemisorption of water and may even lead to structural modifications of the surface. To mimic PEC conditions, we controlled the exposure of the InP surface to water molecules in a precise, pulsed fashion at elevated temperature (200 °C) using an ALD system equipped with UHV sample transfer capabilities. This methodology enables access to surface states that are more representative of a PEC device in operation, as the thermal treatment effectively activates surface reactions and potential desorption processes. The surface composition and electronic structure following pulsed water exposure are determined experimentally using in situ X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) and low-energy electron diffraction (LEED). Near-surface electron dynamics are observed using tr-2PPE, providing information on both valence as well as conduction band states, as well as femtosecond-resolution lifetime information on initially unoccupied states.^[15] Tr-2PPE allows for electronic pathways at the P-rich InP surface to be studied at stages of increasing surface modification, with information on changes to electronic state energies and -lifetimes being trackable. By tracking the electron dynamics on step-wise modified surfaces, we demonstrate that water exposure significantly prolongs the electron lifetimes near the CBM energy level. These observations provide new insights on the energetic and dynamic behavior of photoexcited electrons upon their arrival at surfaces that are chemically and structurally modified by water exposure.

2. Results

2.1. Effects of Water- and Heat Exposure on State Energetics and Surface Structure

Figure 1 and Figure S5 (Supporting Information) show the high-resolution and overview XP spectra, respectively, of the P-rich InP(100) surface before and after one cycle of water exposure, followed by subsequent increasing cycle numbers. After one exposure cycle, no oxygen is observed, indicating that oxygen is not adsorbed on the surface (within the detection limit of the XPS). With an increasing number of water exposure cycles, the intensity of the O 1s core-level increases.

Y. Gao
State Key Laboratory of Catalysis
Dalian Institute of Chemical Physics
Chinese Academy of Sciences
Dalian National Laboratory for Clean Energy
Dalian, P. R. China

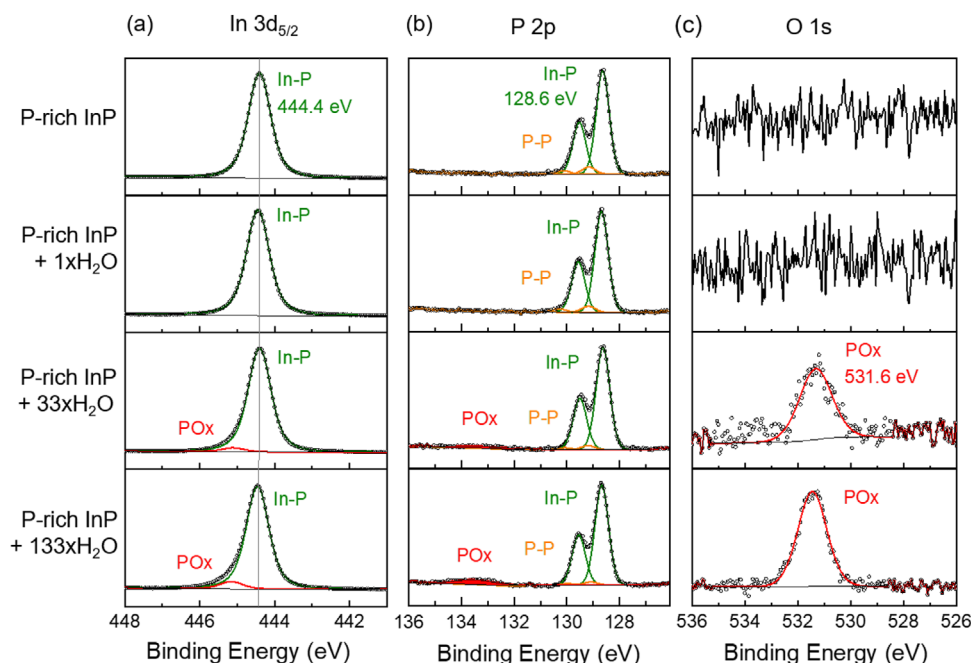


Figure 1. XPS fine spectra of the pure P-rich InP(100) surface in the top row, and with spectra after 1, 33, and 133 cycles of water exposure. The In 3d_{5/2}, P 2p, and O 1s peaks are shown for each stage of surface modification. Indium phosphate compounds are observed from 33 cycles of water exposure, with amplitudes increasing with further water exposure.

In order to analyze the chemical changes on the P-rich InP surface after exposure to water in the ALD chamber, high-resolution XP spectra were taken and fitted. Analysis of the XPS core-levels of In 3d_{5/2} (a), P 2p (b), and O 1s (c) peaks in Figure 1 shows the formation of additional peaks after water exposure. Note that the thermal treatment during water exposure does not alter the surface structure of InP by itself (black curve in Figure S6, Supporting Information). Therefore, the new small peak observed after water exposure originates from the adsorption of and reactions with surface water, and may be related to indium phosphate compounds. In the In 3d_{5/2} core-level in Figure 1a, after exposure to 33 cycles of water, an additional peak forms at 0.7 eV higher binding energy (red line) compared to the peak related to the InP bulk (green line, at 444.4 eV). Peaks near this energy can be related to either InPO₄ (445.05 eV;^[5] 445.7 eV^[36,37]) and/or In(PO₃)₃ (444.75 eV;^[5] 445.4 eV^[36,37]). Additionally, hydroxyl groups may occur on In surface atoms, as calculated previously for the In-rich surface.^[38] On P-rich InP, dissociative water adsorption has been noted to occur in the presence of H vacancies, leading to hydroxyl groups passivating the P dangling bond and forming P–OH bonds.^[17] While there is a finite concentration of H vacancies,^[19] water dissociation is suggested to occur at step edges rather than on terraces, where In dangling bonds are available. The P 2p core-level of the P-rich InP surface (Figure 1b) is fitted with two components, characteristic for this surface, each with a spin-orbit splitting (the ratio of 2p_{3/2} and 2p_{1/2} was fixed to 2:1, and the FWHM of each peak was equal). The larger component is related to In–P bonds, and the smaller surface component to P–P dimers at the surface (yellow line).^[39] The P-rich InP surface is reported in literature to be terminated with a layer of buckled P-dimers each passivated by one hydrogen atom, which form a semiconducting surface with a surface

band gap of 1.34 eV.^[10,19,36,38,40–42] After exposure to 33 cycles, an additional peak at 133.5 eV binding energy is observed (red spectrum). Binding energies of 132.45 and 133.2 eV have been reported for In(PO₃)₃ and InPO₄.^[5] Due to the extremely thin oxide layer, which does not form a complete monolayer based on XPS results, it is not possible to differentiate between these two compounds and their respective contributions. As a result, the spectra are fitted by incorporating only one component at 133.5 eV, which is specifically associated with InPO_x.^[5,18,37,43] A contribution at 531.6 eV in the O 1s core-level, associated with InPO_x (In–O–P bonds in InPO₄ or InPO₃), emerges after 33 cycles (shown in Figure 1c).^[5,18,37,43] A shift toward increased binding energies of the O1s peak by 0.13 eV, from 33 to 133 cycles of water exposure is noticed, corresponding well to increased binding energies of this peak reported for increasing water adsorption.^[17] Indium oxide exhibits In–O–In bonds that are typically visible in the O 1s core-level at binding energies of 530.2 eV in addition to the peak in the In 3d core-level near 444.3 – 444.9 eV.^[5,36,44] Since neither peak is visible in our XP spectra, we can exclude the presence of In₂O₃ at the surface. After exposure to another 100 cycles, the intensity of the peaks related to InPO₄ increases, both in O 1s core-level and in In 3d_{5/2} (see Figure S7, Supporting Information). After 33 cycles, there appears to be a shoulder in emission ≈533–534 eV, which in literature is associated with adsorbed water.^[11,17,45] This feature becomes smaller relative to the phosphate-related peak ≈531.6 eV, indicating that potentially physisorbed water at early exposure stages is desorbed and replaced with oxides.

Before water exposure, the LEED pattern displays spots at half-order, typical for the p(2 × 2)/c(4 × 2) surface reconstruction (Figure 2a). The streaks at half order along [0[−]11] originate from a mixture of p(2 × 2) and c(4 × 2) domains.^[40] After a cycle of

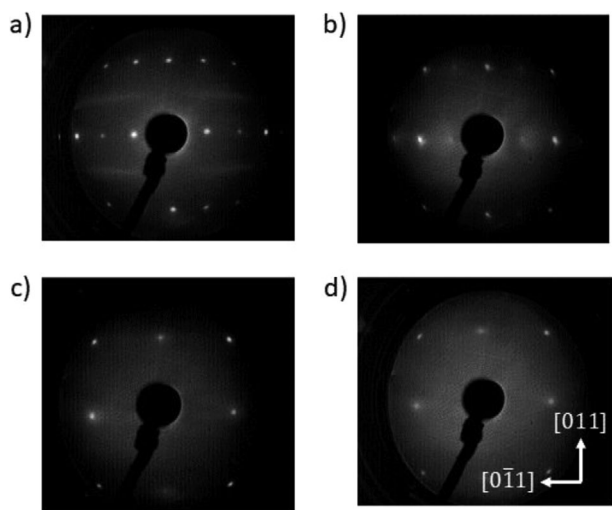


Figure 2. LEED at 80 eV of the P-rich InP surface before water exposure a), after 1 b), 33 c), and 133 cycles d) of water exposure. The P-rich InP surface in (a) shows a characteristic “streaky” (2×1) -like LEED pattern, which is more disordered after a single cycle (b). (c) and (d) show (1×1) surface reconstruction related to the phosphates on the InP surface.

water exposure these streaks are not visible anymore, and only a (2×1) surface reconstruction is observed. The LEED spots are not sharp, and the contrast between them and the background is lower, indicating a reduction of the atomic order on the surface and possibly physisorption of water on the surface. LEED measurements were taken after water exposure within the same UHV system before transfer to the 2PPE UHV system. 2PPE measurements, as discussed below, were repeated and consistent across measurements, showing no evidence of surface changes due to localized laser heating or UHV storage for up to a week during measurements. XPS shows that phosphates were not yet formed on that surface (within the detection limit); also, no clear signature of oxygen is visible (Figure 1b,c, top row). Note that LEED has much higher surface sensitivity (20–200 eV energy range) compared to XPS. Thus, LEED results are more affected by water exposure experiments compared to XPS. The (2×1) LEED pattern indicates that the P–P dimers are preserved on the surface, which is also confirmed by XPS. The P-rich GaP(100) and InP(100) surfaces are known to be rather stable toward water-induced surface modifications,^[12,18,46] due to surface P dimers stabilized by an additional hydrogen atom.^[13,19,40,47,48] This agrees with previous calculations^[17] for single-molecule adsorption as well as the present Density-functional theory (DFT) calculations for water monolayers adsorbed on the P-rich InP surface. As will be discussed below, the physisorption of the water monolayer on the P-rich InP surface essentially preserves the surface structure. Thus, we relate the reduced surface ordering observed here to temporary and reversible physisorption of water or oxygen, as XPS shows no changes in the surface chemistry (no adsorption of either oxygen or water).

After 33 and 133 water exposure cycles, the surface shows a (1×1) surface reconstruction due to the absorbed oxygen on the surface. When heating a separate P-rich InP sample to 200 °C for 1 h without H₂O exposure, the streaky (2×1) -like reconstruction is maintained (Figure S7, Supporting Information). This shows

that the changes observed in LEED are due to the H₂O exposure and not due to the temperature of 200 °C alone. On the P-rich InP(100) surface, two oppositely buckled P-dimers are passivated by one hydrogen atom. This configuration is much less reactive than the In-rich surface termination to water or atmospheric exposure.^[12,18] The (2×1) -like surface reconstruction has been observed even with adsorbed alkyl groups and partial carbon coverage of the surface.^[10,36] It has also been observed in the absence of C or other significant contaminations,^[40,49] indicating good stability of the reconstruction; we had not found any evidence for the presence of carbon on our surfaces (Figure S6, Supporting Information). Chen et al. found the (2×1) -like LEED signature of P-rich InP to persist even after oxidation, whereas the (2×4) In-InP surface changed to a (1×1) LEED pattern after oxygen exposure.^[36] They correlated this to an increased stability to oxidation of the P-rich surface as shown by reflection difference spectroscopy, as well as slower oxygen uptake under increasing temperatures. At 719 °C, phosphorus desorption occurs, which is therefore the upper limit for heating of this surface before the surface reconstructs to the (2×4) configuration.^[36] In combination with XPS results, we hypothesize a two-stage surface modification process, with 1 cycle of water exposure resulting in the physisorption of water primarily, which desorbs and is replaced with surface phosphates during subsequent water exposure steps. This is supported by DFT calculations (Note S2, Supporting Information),^[50–54] which found adsorption energies of 0.21 eV for water, increasing to 0.36 eV for water molecules bonding to pre-adsorbed hydroxyl groups located on P dimers (Figure S14, Supporting Information). As these binding energies exceed $k_B T$ both at room temperature and at 200 °C by about an order of magnitude, water desorption rates likely slow down sufficiently for some water physisorption to persist on the hydroxylated surface before significant oxidation occurs.

Previous work by several of the present authors indicated that while P-rich InP near-surface states are related in part to surface P-dimers, they are in fact spread out over the several uppermost atomic layers and thus represent the sum of the states in these layers.^[32] Based on this, one would not be able to predict a priori to what extent these near-surface states would be modified by water exposure and partial oxidation of the surface P dimer layer. With XPS, we can confirm that surface P-dimers are preserved (Figure 1). Petit et al.^[55] studied the interaction of atomic hydrogen with the naturally formed oxides and contaminations on InP(100). They noted that C and O coverage, which is resistant to thermal desorption, could be removed at 300 °C when combined with H exposure. O and C are only weakly bonded to the surface and are removed after $\approx 10^4$ to 10^5 L of H exposure. At higher exposure, P desorption occurs. Petit et al. measured decreases in the P 2p / In 4d ratio after $\sim 10^6$ L of H exposure, resulting in surface decomposition and formation of metallic indium. Similarly, Stietz et al. performed hydrogen exposure of the P-rich InP(100) surface and also noted decomposition of the surface.^[56] Initially, In-bonds are broken, changing the reconstruction from (2×1) to (4×1) , after which phosphorus desorption occurs, followed by In-droplet formation. They determined P2p/In3d_{3/2} intensity ratios as a function of H exposure. The ratio started dropping at $\approx 10^4$ L H exposure, dropping to half after 10^6 L, and to about a quarter after 10^7 L.^[56] For contaminated samples, changes only appeared to occur at increased H exposures, with P-to-In ratios

starting to drop after $\sim 10^6$ L. Surface phosphorus dangling bonds are already saturated at ≈ 100 L, which is sufficient to ensure complete H termination (and far below values where P desorption occurs).^[56]

Chen et al. reported the reaction of adsorbed oxygen above 450 K, which reacts at 530 K both with P surface dimers as well as with In-P back bonds;^[36] this correlates well with our XPS measurements showing both In-oxide and P-oxide formation after extended water exposure and heating of the surface (Figure 1). Our water exposure was performed at a sample temperature of 473 K and results in the formation of P-oxide (Figure 1), consistent with the peaks observed by Chen et al.^[36]

2.2. Effects of Water Exposure on Ultrafast Electron Dynamics

Our previous tr-2PPE study^[32] revealed the presence of at least nine electronic states, located between the upper end of the valence band and the vacuum energy as shown in Figure 3a,b: six unoccupied surface states labelled as C1 to C6, a near-surface cluster of states identified as a bulk-to-surface transition, a surface state pinning the Fermi level as well as a valence band state labelled V1, see Figure 3.

The emission spectra of the P-rich InP surface after 1, 33 and 133 cycles are given in Figure 3, with data normalized to emission from the bulk-to-surface transition peak (abbreviated as “bulk state” in Figure 3). This feature was attributed in previous work to a cluster of states in the near-surface region, capturing hot electrons photoexcited in the InP bulk and being a key intermediate in their transition to surface states.^[32] Overall emission amplitudes decreased significantly with water exposure, with emission after 133 cycles of water exposure an order of magnitude below emission obtained on the bare P-rich InP surface (Figure S8, Supporting Information). This may be caused in part by scattering of electrons within surface adsorbates and -phosphates, thereby reducing detected emission amplitudes, as well as by suppression of specific surface features due to interactions of surface modifications with the atoms and orbitals causing the respective states. Emission from the bulk-to-surface transition as a sub-surface feature is thus used to normalize emission data to allow for a detailed comparison of emission features. Due to the low per-pulse excitation rates required to avoid space-charge effects and not perturb the near-surface band structure, measurements need to run for several hours. This results in the pump-probe overlap drifting, leading to emission amplitudes dropping throughout measurements. As such, normalizing using sub-surface states allows for measurements to be compared quantitatively. 3D transient plots at each level of water exposure are shown on the left in Figure 3, allowing for overall trends to be tracked visually. The corresponding spectra are given in the right column, showing that all states observed on the bare P-rich InP surface (Figure 3b) are still observed after water exposure of the surface. The shifts of the energetic positions of states of the P-rich InP surface due to water exposure are given in Table S2 (Supporting Information). The energy level of the cluster of states associated with bulk-to-surface transitions (state 7 in Table S2, Supporting Information) shows no significant shift after surface treatment, as the majority of the observed states are related to sub-surface features. In addition to the bulk-to-surface transition, C2, C5, and C6 do not shift ener-

getically (within experimental uncertainty). This is in good agreement with the UPS measurements at P-terminated InP (001) surfaces by Moritz et al.,^[17] where almost no, or only very weak electronic interactions with respect to chemical bond formation with water were observed. The VBM, C1, and C4 shift by -0.2 ± 0.1 eV, with the band gap remaining essentially unchanged. C3 and V1 move by -0.3 ± 0.2 eV, with the relatively large uncertainty due to the reduced amplitude of the peaks. In the case of dissociative water adsorption, traces of OH groups may remain on the surface;^[17] this may contribute to the changes in energetic position or lifetimes of the surface states. Within this scenario, energetically lower-lying surface states are populated via relaxation from higher-energy bulk and surface states. The main scattering mechanism was described previously by Sippel et al.^[57] for In-rich InP (100), where electron capture into surface states and bulk backscattering was in the order of 30 fs and 20 fs, respectively. Further exploration of the relaxation processes for the P-rich InP surface can be found in a previous paper by some of the present authors.^[32]

States C3-5 appear to be suppressed as water exposure increases (Figure 3), consistent with gradual surface oxidation. C6 appears to be less affected, consistent with its previous interpretation of being largely related to features in the fourth atomic layer from the surface and below.^[32] C1 and C2 initially increase at 1 (Figure 3d) and 33 water exposure cycles (f), subsequently decreasing at 133 cycles (h), similarly for emission from the surface state pinning the Fermi level at the mid-gap at the surface. The surface state pinning the Fermi level is cut off by vacuum states, below 0.33 eV before H₂O exposure, and below 0.27 eV after H₂O exposure (Figure 3). Due to this cut-off, any shift in this state's energy cannot be tracked in tr-2PPE. However, He I UPS experiments suggest an increase in work function from 4.39 eV to 4.49 eV after water- and heat exposure of the surface (Figure S8, Supporting Information). “Vacuum states” here refers to the distribution of final states above the vacuum energy, calibrated experimentally by adjusting the sample bias and accounting for the detector's work function. This ensures that the zero kinetic energy corresponds accurately to the sample's vacuum level, independent of any mismatch between the sample and detector work functions.

The apparent suppression of Fermi-level-pinned states is not due to misalignment or detector artifacts. Rather, it reflects a physical effect: surface dipoles and image potential barriers arising from, e.g., adsorbates or surface reconstructions can raise the surface potential barrier, particularly for low-energy electrons near the emission threshold (tens to hundreds of meV). This selectively suppresses the emission of states near E_F , while preserving photoemission from higher-energy states. This observation aligns with density functional theory (DFT) predictions, which suggest that the InP dangling bonds after possible H desorption modify the adsorption behavior of OH, leading to passivation of mid-gap surface states, while not significantly impacting the Fermi level pinning.^[17]

After a single cycle of H₂O exposure of the InP (100) surface (Figure 3c,d), the relative intensities of observed states already differ visually, highlighting how even marginal water exposure with no measurable oxidation in XPS (Figure 1) may already affect the surface noticeably. The most marked difference, visually apparent in Figure 3, is the increased emission of C2 relative to C1 at 33

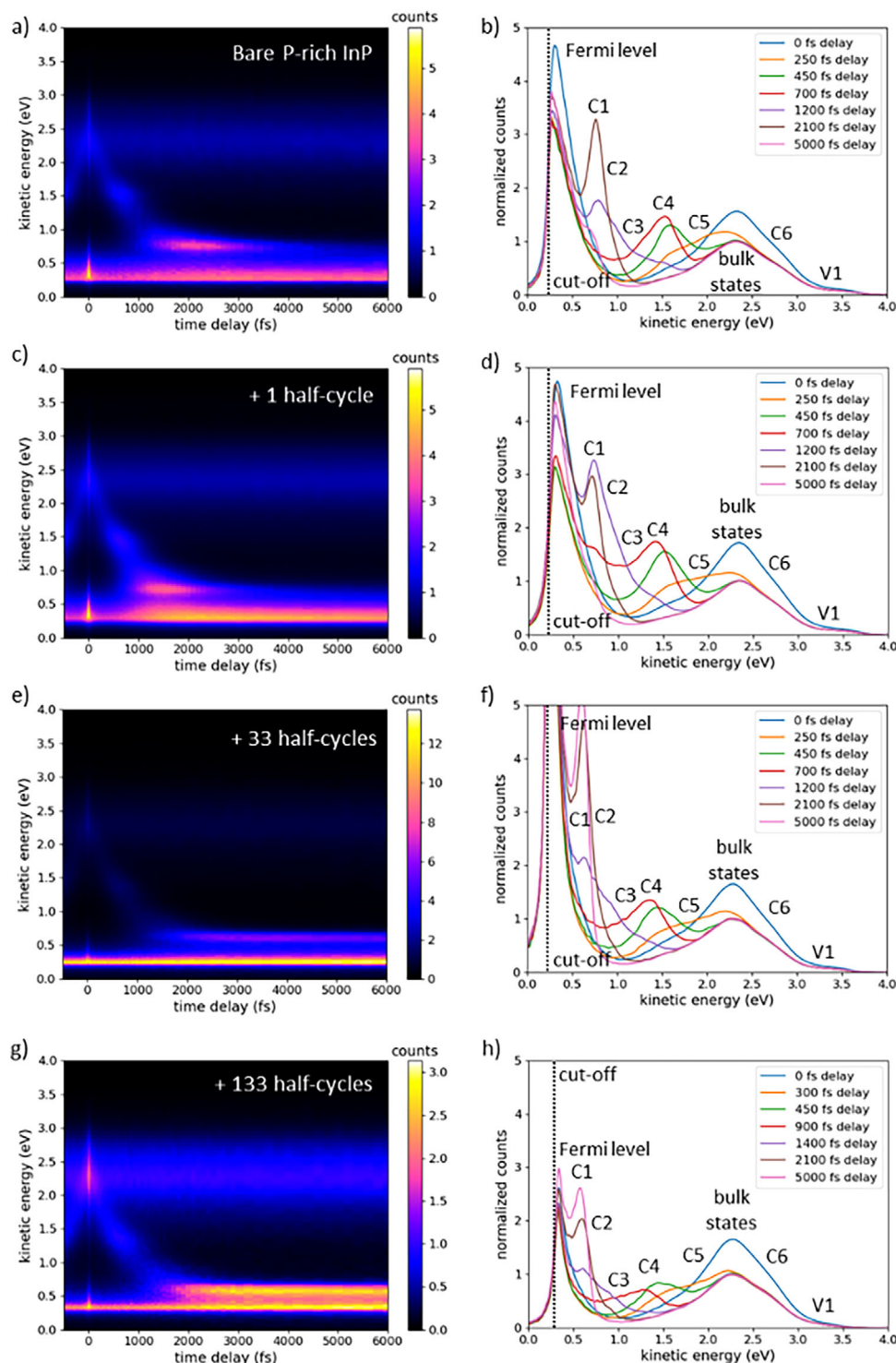


Figure 3. Tr-2PPE transients (a,c,e,g) and the corresponding spectra (b,d,f,h) extracted from the transients of the P-rich InP(100) surface are given; spectra are normalized to the time-independent emission of the bulk state peak. Transients give the count rate of photoelectrons at a range of kinetic energies as a function of time delay between pump and probe pulses. Spectra are taken at a range of time delays and give emission counts of photoelectrons as a function of their kinetic energy at those time delays. Data is given for the P-rich InP surface before water- & heat exposure (a and b), after 1 water exposure cycle (c and d), after 33 (e and f), and after 133 cycles (g and h). The kinetic energy of electrons (corrected for bias potential) is given as a function of time delay between pump and probe. State C1 is significantly extended in lifetime for all surface treatments. Some features after 33 cycles of water exposure (e and f) have moved by ca. 0.2 eV toward lower kinetic energies, and the relative amplitudes of peaks relative to bulk have reduced.

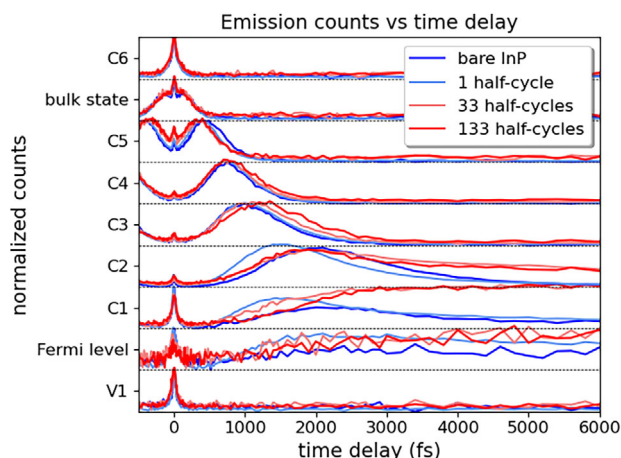


Figure 4. Emission counts as a function of the delay time are given for the previously identified states on P-rich InP (dark blue), and after 1 (light blue), 33 (light red), and 133 cycles (red) of water exposure.

and 133 cycles of water exposure. This corresponds to an increase in lifetime, likely causing the increased emission from C1 and the mid-gap surface state at 33 cycles (Figure 3e,f), before emission is suppressed by the increased oxidation of the surface at 133 cycles. To better understand the detailed modifications with water exposure, we plot the emission from each state as a function of pump-probe delay time (Figure 4). As all near-surface states are preserved after water exposure and subsequent -adsorption and phosphate formation (Figure 1), they can be used as a sensitive probe of surface changes, providing a detailed insight into changes in near-surface ultrafast electron dynamics after water exposure.

The time-dependence of emission from the observed states is depicted in Figure 4, with the bare P-rich InP surface in blue, and the increasing water exposure steps in light blue, light red, and red successively. Emission from C6 and the bulk-to-surface transition cluster of states (“bulk state”) is unchanged within uncertainty, unsurprising given the sub-surface nature of these peaks.^[32] State C5 appears to be filled more quickly after the first water exposure cycle, with peak occupation reached after only $\approx 340 \pm 40$ fs instead of 440 ± 40 fs, with no significant further changes with subsequent cycles. C5 is located closer to the surface (≈ 2 nd vs 4th and above atomic layer) as compared to the bulk state and C6, so it is unsurprising that it is more affected by surface modifications. C4 is not affected as significantly, with peak occupation unchanged at $\approx 750 \pm 40$ fs, and decay times increasing by $\approx 40 \pm 20$ fs, with the precision of this difference limited by how temporally well-defined the flanks of the 30 fs UV pulses are. This is consistent with previous interpretations of C4 being filled only in a small part by electrons relaxing through C5, instead having many photoexcited electrons reaching the P-InP surface around C4 from sub-surface states. This is consistent with the higher emission rates from C4 as compared to C5 and C3. C3 is populated more slowly as water exposure is increased, though as its peak is located in the flank of C4, the uncertainty in its energetic position is increased, which may affect peak occupation times. Nevertheless, an increase in peak emission from $\approx 940 \pm 100$ fs to $\approx 1340 \pm 100$ fs is observed going from the bare surface

to 133 water exposure cycles. C2 is similarly located in the flank of C1 and thus its lifetime cannot be as precisely tracked, however, the peak occupation between the bare surface and 33 as well as 133 cycles is consistent at $\approx 2000 \pm 200$ fs, though relaxation is slowed after water exposure. After 1 water exposure cycle, peak occupation is reached at only $\approx 1500 \pm 100$ fs, this effect carries over to C1 similarly. C1 peak occupation initially decreases from 2400 ± 200 to 2500 ± 100 fs going from the bare surface to 1 water exposure cycle, before increasing to beyond the measured pump-probe limit of 6000 fs. Decay rates of C1 on the bare P-rich InP surface are $\approx 1200 \pm 100$ fs (Figure S11, Supporting Information), and beyond the measurement window after 33 and 133 cycles, indicating a considerable increase in the occupation time of C1, and thus reduced surface recombination rates. This extended lifetime of C1 is the most prominent change observed on the P-rich InP surface after water exposure. It may be beneficial when using the P-rich InP surface in an aqueous electrolyte, as this increase in the time C1 is occupied will bring it closer in timeframe to the surface reaction kinetics of, e.g., PEC reactions.

These observations indicate that the adsorption of surface water and formation of surface phosphates selectively influence the dynamics of excited-state electrons at energy levels closely related to surface reactions. As all observed near-surface states are in part related to sub-surface features, the fact that C1 at the surface CBM is more strongly affected than other states may point to a reduced recombination rate in the near-surface region being a significant contributor to observed changes.

To complement the experimental observations and gain further insight into the mechanisms underlying surface state lifetime changes, we performed density functional theory (DFT) and ab initio molecular dynamics (AIMD) calculations on the excited-state dynamics of the P-rich InP(100) surface under the influence of adsorbed water.^[58,59] These simulations modeled the experimentally observed (2×2) -2D-2H reconstruction and included both a single water monomer and a hydrogen-bonded overlayer of nine H_2O molecules per (2×2) unit cell; results are provided in Note S2, Figures S13, and S14 (Supporting Information).^[60] The modelled structures represent the early stages of surface modification upon water exposure, where XPS indicates little or no phosphate formation (Figure 1c). Due to the highly disordered, amorphous, and structurally variable nature of phosphate-terminated surfaces as evidenced by the (1×1) LEED pattern after 35 and 135 pulses (Figure 2c,d), comparable simulations were not feasible for these oxidized structures. Instead, we focused on the water-adsorbed systems to extract fundamental insights into how surface adsorbates influence ultrafast surface carrier dynamics.

Our DFT calculations reveal that adsorption of water, even in sub-monolayer form, does not significantly perturb the electronic structure of the InP surface: the energies, dispersions, and orbital character of surface states such as C1 and C2 remain nearly unchanged. However, AIMD simulations on excited-state potential energy surfaces show a marked effect of water coverage on vibrational dynamics, resulting in significant changes to electron lifetimes at C1. The simulations were initialized by exciting an electron from the highest occupied surface state (V1, Figure 3) to the surface-localized conduction band state C1. On the bare P-rich InP surface, transitions out of C1 are related to strong vertical vibrational modes of surface phosphorus atoms, especially

those in P–P dimers. Adsorbed water, particularly as a hydrogen-bonded overlayer, dampens both vibrational modes and also reduces the amplitude of dimer-stretching oscillations, reducing non-radiative recombination and significantly prolonging the occupancy of C1 in most simulated trajectories.

These results indicate that water adsorption after initial water exposure suppresses key surface phonon modes that mediate nonadiabatic transitions between near-surface electronic states around the band-gap.^[61,62] Since the overall geometry and band structure of the surface remain intact, the increased lifetime is not a consequence of static electronic passivation of electronic transition channels, but of vibrational decoupling. This explains why C1 lifetimes increase after only a single water pulse (Figure 3c,d), when no phosphate peak is detected in XPS yet (Figure 1c). Our results therefore provide a microscopic explanation for the observed early-stage dynamics and validate the interpretation that vibrational coupling can govern carrier decay at the interface.

As water exposure increases to 33 and 133 cycles, XPS shows the emergence of a phosphate peak near 531.6 eV and the disappearance of the high-binding-energy shoulder assigned to molecular H₂O (Figure 1c). The LEED data change to a (1 × 1) pattern, indicating structural disorder, while tr-2PPE shows continued increases in C1 lifetime (Figures 3f,h and 4). These trends suggest that phosphate formation contributes further to vibrational damping at the surface. Phosphate species likely add mass and bonding complexity to the surface layer, thereby disrupting coherent phonon modes. Suppression of such vibrations may hinder nonradiative transitions and thereby sustain long-lived excited states near the CBM.^[63] Phosphates may then play a similar dynamical role to that of physisorbed water, reducing non-radiative transition rates by limiting coupling between vibrational and electronic degrees of freedom.

Together, these results support a two-stage model of surface modification upon water exposure: an initial regime in which water adsorption at trench or defect sites damps surface phonons and extends near-surface CBM lifetimes, and a subsequent regime in which chemically bound phosphate species further suppress vibrational motion and increase lifetimes further. Surface oxidation, especially in amorphous layers, is often assumed to degrade carrier transport and increase recombination rates. Our findings suggest that some surface oxidation terminations, particularly those that lead to localized mass on a still-existing surface layer, such as the P–P dimer surface here, or that break vibrational coherence, can improve near-surface state lifetimes by attenuating decay pathways. This dynamical perspective demonstrates the importance of factors beyond static band alignment and structure analysis, and has implications for optimizing III–V surfaces in photoelectrochemical and photovoltaic devices.

3. Conclusion

Changes in the electron excitation dynamics and charge carrier pathways of the c(4×2)/p(2×2)-reconstructed P-rich InP(100) surfaces before and after H₂O exposure were studied in depth experimentally, and related to DFT results. Water adsorption and phosphate formation was shown to significantly increase the lifetime of the InP C1 state at the surface CBM, thereby indicating reduced surface recombination, while only weakly affecting

other states. This lifetime enhancement correlates with progressive surface modification: initial water adsorption at low exposures, followed by phosphate formation at higher doses, as supported by LEED symmetry changes from (2 × 1)-like to (1 × 1) and XPS core-level evolution.

Excited-state DFT calculations reveal that water adsorption suppresses vertical and dimer-stretching surface vibrations, which are shown to couple strongly to the C1 state and mediate its decay. This vibrational damping leads to a clear increase in excited carrier lifetimes at C1, even in the absence of electronic structure changes. As phosphate species form at higher water doses, we observe a further increase in lifetime at C1, which we attribute to continued vibrational suppression. In the case of phosphates, this is likely related to the added mass and structural disorder of the oxidized layer. These two regimes, first H₂O physisorption and then oxidation, thus appear to contribute sequentially and cumulatively to the stabilization of near-surface excited carriers.

This finding challenges the conventional assumption that surface oxidation universally increases recombination rates, and thereby degrades interface performance. Instead, our finding suggest that under the right conditions, surface adsorbates or even amorphous oxidation products may reduce recombination rates by suppressing phonon-mediated decay channels, without altering favorable electronic alignments. The increased lifetime at the near-surface CBM may allow for these surface states to affect operando device behavior of, for example, an InP-based PEC cell significantly more strongly than can be estimated from the UHV state lifetimes. These insights demonstrate the need to consider vibrational coupling in addition to the band structure when evaluating surface and interface quality.

By combining ultrafast spectroscopy with surface-sensitive structural and chemical probes, and validating key mechanisms with atomistic simulations, we were able to use the P-rich InP surface as a reference surface to better understand how aqueous exposure modifies III–V semiconductor surfaces. The identified mechanism of CBM lifetime enhancement via molecule adsorption and oxide formation opens new possibilities for engineering carrier dynamics at III–V optoelectronic and photoelectrochemical device interfaces.

4. Experimental Section

Sample Preparation: Metalorganic vapor phase epitaxy (MOVPE) was used to prepare the p(2×2)/c(4×2)-reconstructed P-terminated InP(100) surfaces. The surfaces were grown on p-doped InP substrates with a doping concentration of $2 \times 10^{18} \text{ cm}^{-3}$ (Zn-doped) and a 0.1° miscut toward the [111] direction. The procedure is explained in detail in ref.^[32] the structure of the surface reconstruction is shown in Figure S2 (Supporting Information), which is reprinted from.^[32] Modification of the P-rich InP surface was performed in a setup designed for atomic layer deposition (ALD). A typical ALD process consist of a combination of two half-cycles, one for the deposition of the metal precursor, and the other one for the oxidation of this precursor with, e.g., water. In this study, it only uses the second part of the cycle to finely control the exposure of InP to water. To investigate the charge carrier dynamics, as well as the stability and surface kinetics of the MOVPE-grown InP (100) samples under water- & heat exposure as part of the ALD process, it conducted tr-2PPE and XPS (Specs Focus 500 and Phoibos 100, Al K α radiation, 1486.74 eV) measurements on samples exposed only to water. Each water exposure

cycle consists of exposure to a water vapor pressure of 1 mbar for 1.5 s, followed by a 0.1 s argon purge to maintain consistent conditions between cycles; more details can be found in Table S1 (Supporting Information). The substrate temperature was kept at 200 °C during these cycles. The XP spectra were measured at 90° photoelectron take-off angle with a pass energy of 10 eV and energy steps of 0.1 eV. The ALD, XPS, and UPS chambers were all part of the same UHV system, which also allowed for UHV sample transfer to the (separate) tr-2PPE system. The sample was measured after 1, 33, and 133 water exposure cycles, resulting in a cumulative H₂O exposure of 1.1×10^6 L, 3.7×10^7 L, and 1.5×10^8 L, respectively.

Time-Resolved Two-Photon Photoemission Spectroscopy: Time-resolved two-photon photoemission (tr-2PPE) photoexcites electrons from occupied electronic states in the valence band or defect or surface states in the band-gap using a pump pulse. These hot electrons then thermalize into unoccupied states (Figures S1 and S2, Supporting Information). After a time delay set by a computer-controlled delay stage, a probe pulse photon emits the electrons, which were then detected by a time-of-flight (TOF) spectrometer (Figure S3, Supporting Information). By scanning the time delay between the pump and probe pulses and analyzing the resulting kinetic energy distribution, information on electronic energy levels and their lifetimes can be deduced. The information depth of tr-2PPE was limited by the inelastic mean free path of electrons. In previous studies in our group, the information depth of InP(100) was estimated to be 45 Å,^[64] corresponding to about eight atomic layers of the InP crystal. This allows for observation of bulk and surface features as well as transitions between bulk and surface states.

In the near-surface region, electron dynamics can be tracked through both occupied and unoccupied states near the band gap, with particular focus on unoccupied conduction band states, which were not accessible to single-photon spectroscopic methods such as XPS and UPS.^[65,66] By varying the photon energies of the pump and probe, it can change the energy levels accessed by the pumped electrons. This variation also induces an asymmetry in the time-domain response around the zero-delay point when using pump and probe beams of different photon energies. A detailed description of the experimental parameters is given in.^[32] All spectroscopic (2PPE, XPS, UPS) and LEED measurements were performed at room temperature (20.6 ± 0.2 °C).

Typically, visible light (VIS) pump pulses were adjusted to ≈ 533 nm (2.33 eV) with a pulse energy of 3.3 nJ at a full width at half maximum (FWHM) of 40 fs at the sample. Ultraviolet (UV) pump and probe beams were tuned to ≈ 276 nm (4.49 eV) with a FWHM of 30 fs. The UV pump was usually calibrated to 0.27 nJ pulse energy, while the UV probe was set to ≈ 0.13 nJ. A TOF detector with a 7.3° acceptance angle was positioned 3–5 mm from the sample surface to detect photoemitted electrons and record their kinetic energies, with an uncertainty of ≈ 50 meV. The angle of incidence on the sample for both the pump and probe beams was maintained at 45°. The pump and probe intensities were adjusted to avoid surface charging and to minimize the effect on electron dynamics at higher emission rates. Both pump and probe pulses were p-polarized in all measurements used in the present work. The peaks in the resulting tr-2PPE spectra were analyzed with a Python script assuming Voigt peak shapes, as detailed in our previous study^[32] (Figure S4, Supporting Information). Voigt peaks account for both Gaussian contributions to peak width due to the energy distribution of photons and the instrument response as the major factors, as well as accounting for smaller, but not insignificant, Lorentzian contributions. The latter were mainly due to electronic state lifetimes, local energy levels due to inhomogeneities, and limited lifetimes of final states of emitted electrons.^[67,68] Data slices were obtained by taking time delays where the states were particularly pronounced, and averaging out over a few adjacent delay slices in raw data.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank Wolfram Jaegermann for helpful discussions. The authors are grateful to acknowledge the financial support of German Research Foundation (DFG project PAK 981, project no. FR 4025/2-1, KR4816/1-1, HA3096/14-1, TRR 142/3-2024—Project Numbers 231447078 and SCHM1361/33). The authors thank the Paderborn Center for Parallel Computing and the Höchstleistungs-Rechenzentrum Stuttgart (HLRS) for grants of high-performance computer time. The authors also express gratitude for financial support provided by the German Federal Ministry of Research, Technology and Space (BMFTR, H2Demo project no. 03SF0619) and Carl Zeiss Stiftung (Funding code: P2023-02-008). A.P. acknowledges funding from the BMFTR (SINATRA: PARASOL, project no. 033RC037).

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

All authors have given approval to the final version of the manuscript.

Data Availability Statement

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

Keywords

carrier dynamics, energy, photoelectrochemistry, semiconductors, surface science

Received: May 26, 2025

Revised: June 28, 2025

Published online:

- [1] W.-H. Cheng, M. H. Richter, M. M. May, J. Ohlmann, D. Lackner, F. Dimroth, T. Hannappel, H. A. Atwater, H.-J. Lewerenz, *ACS Energy Lett.* **2018**, *3*, 1795.
- [2] X. Yin, C. Battaglia, Y. Lin, K. Chen, M. Hettick, M. Zheng, C.-Y. Chen, D. Kiriya, A. Javey, *ACS Photonics* **2014**, *1*, 1245.
- [3] L. Gao, Y. Cui, R. H. J. Vervuurt, D. van Dam, R. P. J. van Veldhoven, J. P. Hofmann, A. A. Bol, J. E. M. Haverkort, P. H. L. Notten, E. P. A. M. Bakkers, E. J. M. Hensen, *Adv. Funct. Mater.* **2016**, *26*, 633.
- [4] M. H. Lee, K. Takei, J. Zhang, R. Kapadia, M. Zheng, Y.-Z. Chen, J. Nah, T. S. Matthews, Y.-L. Chueh, J. W. Ager, A. Javey, *Angew. Chem., Int. Ed.* **2012**, *51*, 10760.
- [5] A. G. Muñoz, C. Heine, M. Lublow, H. W. Klemm, N. Szabó, T. Hannappel, H.-J. Lewerenz, *ECS J. Solid State Sci. Technol.* **2013**, *2*, Q51.
- [6] D. E. Aspnes, A. A. Studna, *Phys. Rev. B* **1983**, *27*, 985.
- [7] J. Wang, F. Sciarrino, A. Laing, M. G. Thompson, *Nat. Photonics* **2020**, *14*, 273.
- [8] M. Smit, K. Williams, J. van der Tol, *APL Photonics* **2019**, *4*, 050901.
- [9] Y. Wang, Y. Jiao, K. Williams, *APL Photonics* **2024**, *9*, 050902.
- [10] L. Li, B.-K. Han, Q. Fu, R. F. Hicks, *Phys. Rev. Lett.* **1999**, *82*, 1879.
- [11] B. C. Wood, E. Schwegler, W. I. Choi, T. Ogitsu, *J. Phys. Chem. C* **2014**, *118*, 1062.

- [12] M. M. May, O. Supplie, C. Höhn, R. van de Krol, H.-J. Lewerenz, T. Hannappel, *New J. Phys.* **2013**, *15*, 103003.
- [13] P. Kleinschmidt, H. Döscher, P. Vogt, T. Hannappel, *Phys. Rev. B* **2011**, *83*, 155316.
- [14] A. G. Muñoz, C. Heine, H. W. Klemm, T. Hannappel, N. Szabo, H.-J. Lewerenz, *ECS Trans.* **2011**, *35*, 141.
- [15] Y. Lin, R. Kapadia, J. Yang, M. Zheng, K. Chen, M. Hettick, X. Yin, C. Battaglia, I. D. Sharp, J. W. Ager, A. Javey, *J. Phys. Chem. C* **2015**, *119*, 2308.
- [16] E. Aharon-Shalom, A. Heller, *J. Electrochem. Soc.* **1982**, *129*, 2865.
- [17] D. C. Moritz, I. A. Ruiz Alvarado, M. A. Zare Pour, A. Paszuk, T. Frieß, E. Runge, J. P. Hofmann, T. Hannappel, W. G. Schmidt, W. Jaegermann, *ACS Appl. Mater. Interfaces* **2022**, *14*, 47255.
- [18] M. M. May, H.-J. Lewerenz, T. Hannappel, *J. Phys. Chem. C* **2014**, *118*, 19032.
- [19] R. Sciotto, I. A. Ruiz Alvarado, W. G. Schmidt, *Surfaces* **2024**, *7*, 79.
- [20] M. Löw, M. Guidat, J. Kim, M. M. May, *RSC Adv.* **2022**, *12*, 32756.
- [21] Z. Xu, B. Hou, F. Zhao, Z. Cai, H. Shi, Y. Liu, C. L. Hill, D. G. Musaev, M. Mecklenburg, S. B. Cronin, T. Lian, *Nano Lett.* **2021**, *21*, 8017.
- [22] J. L. Young, M. A. Steiner, H. Döscher, R. M. France, J. A. Turner, T. G. Deutsch, *Nat. Energy* **2017**, *2*, 17028.
- [23] A. Heller, R. G. Vadimsky, *Phys. Rev. Lett.* **1981**, *46*, 1153.
- [24] S. Hu, M. R. Shaner, J. A. Beardslee, M. Lichterman, B. S. Brunschwig, N. S. Lewis, *Science* **2014**, *344*, 1005.
- [25] D. Bae, S. Shayestehaminzadeh, E. B. Thorsteinsson, T. Pedersen, O. Hansen, B. Seger, P. C. K. Vesborg, S. Ölafsson, I. Chorkendorff, *Sol. Energy Mater. Sol. Cells* **2016**, *144*, 758.
- [26] B. Seger, T. Pedersen, A. B. Laursen, P. C. K. Vesborg, O. Hansen, I. Chorkendorff, *J. Am. Chem. Soc.* **2013**, *135*, 1057.
- [27] B. Mei, T. Pedersen, P. Malacrida, D. Bae, R. Frydendal, O. Hansen, P. C. K. Vesborg, B. Seger, I. Chorkendorff, *J. Phys. Chem. C* **2015**, *119*, 15019.
- [28] B. Abendroth, T. Moebus, S. Rentrop, R. Strohmeier, M. Vinnichenko, T. Weling, H. Stöcker, D. C. Meyer, *Thin Solid Films* **2013**, *545*, 176.
- [29] A. J. Kaufman, R. A. Krivina, M. Shen, S. W. Boettcher, *ACS Energy Lett.* **2022**, *7*, 541.
- [30] J. Gu, Y. Yan, J. L. Young, K. X. Steirer, N. R. Neale, J. A. Turner, *Nat. Mater.* **2015**, *15*, 456.
- [31] T. Moehl, J. Suh, L. Sévry, R. Wick-Joliat, S. D. Tilley, *ACS Appl. Mater. Interfaces* **2017**, *9*, 43614.
- [32] J. Diederich, J. Velasquez Rojas, M. A. Zare Pour, I. A. Ruiz Alvarado, A. Paszuk, R. Sciotto, C. Höhn, K. Schwarzburg, D. Ostheimer, R. Eichberger, W. G. Schmidt, T. Hannappel, R. van de Krol, D. Friedrich, *J. Am. Chem. Soc.* **2024**, *146*, 8949.
- [33] R. W. Johnson, A. Hultqvist, S. F. Bent, *Mater. Today* **2014**, *17*, 236.
- [34] J. Diederich, J. V. Rojas, A. Paszuk, M. A. Z. Pour, C. Höhn, I. A. R. Alvarado, K. Schwarzburg, D. Ostheimer, R. Eichberger, W. G. Schmidt, T. Hannappel, R. van de Krol, D. Friedrich, *Adv. Funct. Mater.* **2024**, *34*, 2409455.
- [35] J. Cen, Q. Wu, M. Liu, A. Orlov, *Green Energy & Environ.* **2017**, *2*, 100.
- [36] G. Chen, S. B. Visbeck, D. C. Law, R. F. Hicks, *J. Appl. Phys.* **2002**, *91*, 9362.
- [37] H. J. Lewerenz, K. H. Schulte, *Electrochim. Acta* **2002**, *47*, 2639.
- [38] I. A. Alvarado Ruiz, W. G. Schmidt, *ACS Omega* **2022**, *7*, 19355.
- [39] P. Vogt, A. M. Frisch, T. h. Hannappel, S. Visbeck, F. Willig, C. Jung, R. Follath, W. Braun, W. Richter, N. Esser, *Appl. Surf. Sci.* **2000**, *166*, 190.
- [40] W. G. Schmidt, P. H. Hahn, F. Bechstedt, N. Esser, P. Vogt, A. Wange, W. Richter, *Phys. Rev. Lett.* **2003**, *90*, 126101.
- [41] A. Goryachev, L. Gao, R. P. J. van Veldhoven, J. E. M. Haverkort, J. P. Hofmann, E. J. M. Hensen, *Phys. Chem. Chem. Phys.* **2018**, *20*, 14242.
- [42] T. Hannappel, L. Töben, K. Möller, F. Willig, *J. Electron. Mater.* **2001**, *30*, 1425.
- [43] G. Hollinger, E. Bergignat, J. Joseph, Y. Robach, *J. Vac. Sci. Technol. A* **1985**, *3*, 2082.
- [44] X. Zhang, T. A. Pham, T. Ogitsu, B. C. Wood, S. Ptasińska, *J. Phys. Chem. C* **2020**, *124*, 3196.
- [45] M. A. Henderson, *ChemInform* **2002**, *33*, 228.
- [46] M. M. May, O. Supplie, C. Höhn, W.-D. Zabka, H.-J. Lewerenz, R. van de Krol, T. Hannappel, *Sol. Hydrog. Nanotechnol. VIII* **2013**, *46*, 88220M.
- [47] T. Hannappel, S. Visbeck, K. Knorr, J. Mahrt, M. Zorn, F. Willig, *Appl. Phys. A* **1999**, *69*, 427.
- [48] G. Chen, S. F. Cheng, D. Tobin, L. Li, K. Raghavachari, R. F. Hicks, *Phys. Rev. B* **2003**, *68*, 121303.
- [49] M. Faur, M. Faur, D. T. Jayne, M. Goradia, C. Goradia, *Surf. Interface Anal.* **1990**, *15*, 641.
- [50] O. Pankratov, M. Scheffler, *Phys. Rev. Lett.* **1995**, *75*, 701.
- [51] E. Artacho, M. Rohlfing, M. Côté, P. D. Haynes, R. J. Needs, C. Molteni, *Phys. Rev. Lett.* **2004**, *93*, 116401.
- [52] M. L. Tiago, S. Ismail-Beigi, S. G. Louie, *Phys. Rev. B* **2004**, *69*, 125212.
- [53] J. C. Tully, *J. Chem. Phys.* **1990**, *93*, 1061.
- [54] E. Pradhan, K. Sato, A. V. Akimov, *J. Phys. Condens. Matter* **2018**, *30*, 484002.
- [55] E. J. Petit, F. Houzay, J. M. Moison, *Surf. Sci.* **1992**, *269–270*, 902.
- [56] F. Stietz, J. Woll, V. Persch, T. Allinger, W. Erfurth, A. M. Goldmann, J. A. Schaefer, *Phys. Status Solidi A* **1997**, *159*, 185.
- [57] P. Sippel, Electronic Structure and Electron Dynamics in Semiconductor Materials for New Photovoltaic Applications, Ph.D. Thesis, Technische Universität Ilmenau, Ilmenau, Germany **2015**, *1*.
- [58] T. Frigge, B. Hafke, T. Witte, B. Krenzer, C. Streubühr, A. Samad Syed, V. Mikšić Trontl, I. Avigo, P. Zhou, M. Ligges, D. von der Linde, U. Bovensiepen, M. Horn-von Hoegen, S. Wippermann, A. Lücke, S. Sanna, U. Gerstmann, W. G. Schmidt, *Nature* **2017**, *544*, 207.
- [59] C. W. Nicholson, A. Lücke, W. G. Schmidt, M. Puppig, L. Rettig, R. Ernstorfer, M. Wolf, *Science* **2018**, *362*, 821.
- [60] L. J. Glahn, I. A. Ruiz Alvarado, S. Neufeld, M. A. Zare Pour, A. Paszuk, D. Ostheimer, S. Shekarabi, O. Romanyuk, D. C. Moritz, J. P. Hofmann, W. Jaegermann, T. Hannappel, W. G. Schmidt, *Phys. Status Solidi B* **2022**, *259*, 2200308.
- [61] Z.-F. Xu, C.-J. Tong, R. Si, G. Teobaldi, L.-M. Liu, *J. Phys. Chem. Lett.* **2022**, *13*, 857.
- [62] L. Zhang, Q. Zheng, Y. Xie, Z. Lan, O. V. Prezhdo, W. A. Saidi, J. Zhao, *Nano Lett.* **2018**, *18*, 1592.
- [63] J. van Engelen, S. Reniers, J. Bolk, K. Williams, J. van der Tol, Y. Jiao, In 2019 Compound Semiconductor Week (CSW), Nara, Japan, May **2019**.
- [64] L. Töben, T. Hannappel, R. Eichberger, K. Möller, L. Gundlach, R. Ernstorfer, F. Willig, *J. Cryst. Growth* **2003**, *248*, 206.
- [65] H. Ueba, B. Gumhalter, *Dyn. Electron Transf. Process. Surf.* **2007**, *82*, 193.
- [66] M. Borgwardt, S. T. Omelchenko, M. Favaro, P. Plate, C. Höhn, D. Abou-Ras, K. Schwarzburg, R. van de Krol, H. A. Atwater, N. S. Lewis, R. Eichberger, D. Friedrich, *Nat. Commun.* **2019**, *10*, 2106.
- [67] P. M. A. Sherwood, *Surf. Interface Anal.* **2019**, *51*, 254.
- [68] H. Petek, S. Ogawa, *Prog. Surf. Sci.* **1997**, *56*, 239.

ADVANCED MATERIALS INTERFACES

Open Access

Supporting Information

for *Adv. Mater. Interfaces*, DOI 10.1002/admi.202500463

Ultrafast Electron Dynamics at the Water-Modified InP(100) Surface

*Jonathan Diederich, Agnieszka Paszuk, Isaac Azahel Ruiz Alvarado, Marvin Krenz, Mohammad Amin Zare Pour, Diwakar Suresh Babu, Jennifer Velazquez Rojas, Christian Höhn, Yuying Gao, Klaus Schwarzburg, David Ostheimer, Rainer Eichberger, Wolf Gero Schmidt, Thomas Hannappel, Roel van de Krol and Dennis Friedrich**

Ultrafast electron dynamics at the water-modified InP(100) surface

Jonathan Diederich^{a,c,g}, Agnieszka Paszuk^{b,c}, Isaac Azahel Ruiz Alvarado^d, Marvin Krenz^d, Mohammad Amin Zare Pour^{b,c}, Diwakar Suresh Babu^{a,c}, Jennifer Velazquez Rojas^{a,e}, Christian Höhn^a, Yuying Gao^{a,f}, Klaus Schwarzburg^a, David Ostheimer^b, Rainer Eichberger^{a,b}, Wolf Gero Schmidt^d, Thomas Hannappel^b, Roel van de Krol^{a,c}, Dennis Friedrich^{a*}

^a Institute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany

^b Fundamentals of Energy Materials, Institute of Physics, Technische Universität Ilmenau, 98693 Ilmenau, Germany

^c BMFTR Junior Research Group PARASOL, Institute of Physics, Technische Universität Ilmenau, 98693 Ilmenau, Germany

^d Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33095 Paderborn, Germany

^e Institut für Chemie, Technische Universität Berlin, 10623 Berlin, Germany

^f State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian, P. R. China

^g Current address: Frick Chemistry Laboratory, Princeton University, NJ-08544 Princeton, United States of America

ASSOCIATED CONTENT

SUPPLEMENTARY INFORMATION

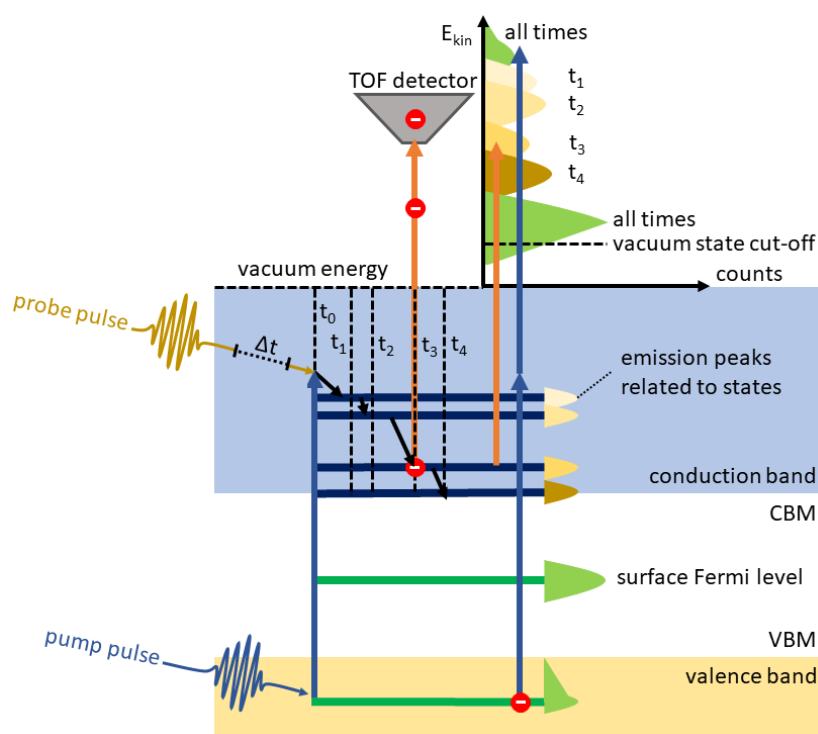


Fig. S1: Schematic showing the excitation and emission pathways for tr-2PPE, re-printed from 33. Electrons are photoexcited from occupied states in the valence band, or surface states in the band gap by a pump pulse at $t=0$. Photoexcited electrons thermalize through conduction band states, from where they are photoemitted by a probe pulse after a variable time delay. By scanning over time delay and recording the kinetic energies of electrons in a TOF detector, electron relaxation paths and electronic band structure in the near-surface region are obtained.

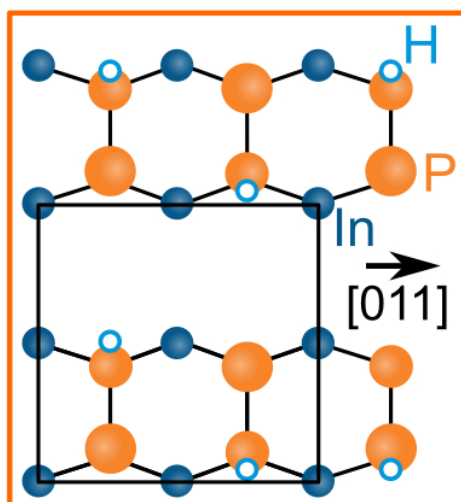


Fig. S2: Schematic surface reconstruction of the P-terminated InP(100) $p(2 \times 2)/c(4 \times 2)$ surface reconstruction. The $p(2 \times 2)$ unit cell is highlighted by the black square, with adjacent P–P dimers rows arranged in-phase; the $c(4 \times 2)$ unit cell is not shown here. Image reproduced under terms of the CC-BY 4.0 license. [33], 2024, published by American Chemical Society.

Table S1: The two steps in the table make up one exposure cycle. Pulse- and purge durations for the sequential steps are shown, consisting of alternating H_2O and an argon pump/purge/pump step, which allows for consistent pressure and reaction conditions throughout the many cycles performed.

ALD process description	Pulse duration (s)	Purge duration (s)
H_2O	1.5	30
Argon	0.1	30

Table S2: Measured kinetic energies and corresponding energy levels vs vacuum of the P-rich InP surface before and after water exposure. Uncertainties in kinetic energies due to the TOF detector are 0.05 eV, with additional uncertainty due to partial overlap of the peaks (Fig. S4). Surface state positions are correlated to UPS work function measurements (Fig. S8). A small negative shift in state energies is observed after water exposure, which is largely within uncertainty, but may be related to weak surface polarization effects induced by hydroxyl groups generated after hydrogen desorption in UHV.

State	State name	E_{kin} on pure surface (eV)	Position	E_{kin} after 133 H ₂ O cycles (eV)	Position	Difference (eV)
1	Surface state pinning the Fermi level	cut-off 0.27 ± 0.05	from UPS: -4.39 ± 0.05	Cut-off below 0.33 ± 0.05	from UPS: -4.49 ± 0.05	-0.10 ± 0.10
2	C1	0.77 ± 0.05	-3.72 ± 0.05	0.61 ± 0.05	-3.88 ± 0.05	-0.16 ± 0.10
3	C2	1.00 ± 0.10	-3.49 ± 0.10	0.92 ± 0.10	-3.57 ± 0.10	-0.08 ± 0.20
4	C3	1.35 ± 0.10	-3.14 ± 0.10	1.11 ± 0.10	-3.47 ± 0.10	-0.24 ± 0.20
5	C4	1.56 ± 0.05	-2.93 ± 0.05	1.37 ± 0.05	-3.12 ± 0.05	-0.19 ± 0.10
6	C5	1.95 ± 0.10	-2.54 ± 0.10	1.89 ± 0.10	-2.60 ± 0.10	-0.06 ± 0.20
7	bulk	2.33 ± 0.05	-2.16 ± 0.05	2.28 ± 0.05	-2.21 ± 0.05	-0.05 ± 0.10
8	C6	2.80 ± 0.10	-1.69 ± 0.10	2.72 ± 0.10	-1.77 ± 0.10	-0.08 ± 0.20
9	V1	3.43 ± 0.10	-5.55 ± 0.10	3.11 ± 0.10	-1.38 ± 0.10	-0.32 ± 0.20
	VBM	3.85 ± 0.10	-5.13 ± 0.10	3.65 ± 0.10	-5.33 ± 0.10	-0.20 ± 0.20

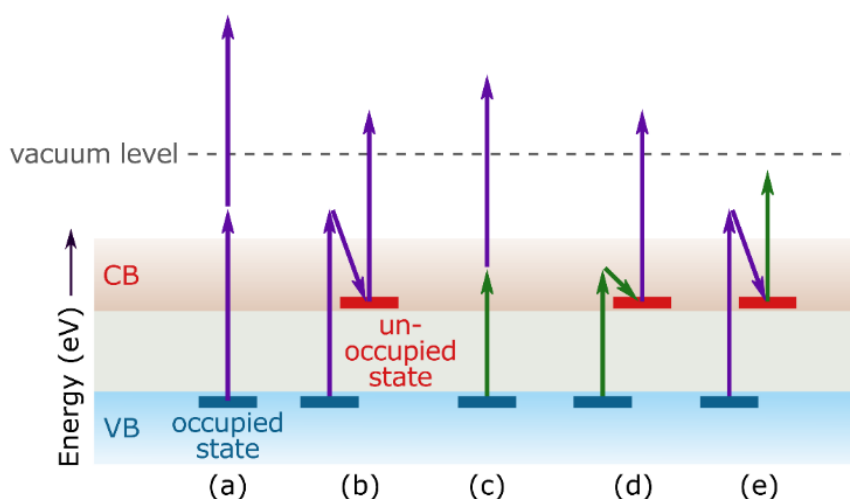


Fig. S3: Schematic of two-photon photoemission using two different frequencies as pump or probe (to scale for 276 nm UV and 533 nm VIS), re-printed from ³³. In a), two UV photons are incident simultaneously, in b) a UV photon photoexcites an electron, which decays down to the next-lowest state and is emitted from there by a second UV photon. c) and d) show a combination of two different photon energies. In c), a VIS photon pumps an electron which is emitted by a UV photon. In e) an electron is pumped by the UV photon, but then thermalizes too much energy before incidence of the VIS photon, and no emission of electrons is observed.

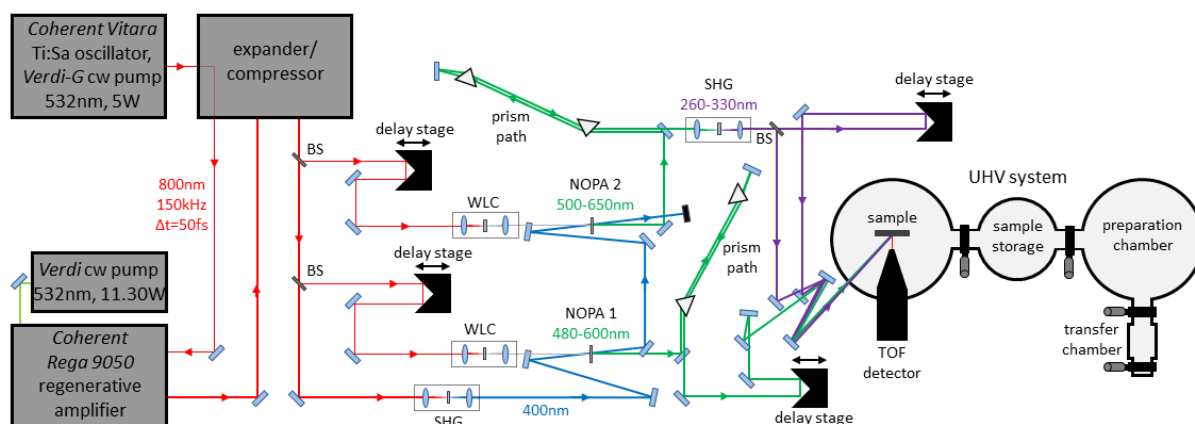


Fig. S4: Schematic of the overall tr-2PPE set-up, simplified to enhance presentation, re-printed from ³³. The pulse-generating and -amplifying elements are on the left, NOPA 1 and 2 including 800nm to 400nm SHG in the middle. A prism path after each NOPA is shown, the output of NOPA 1 serves as the VIS pump, the output of NOPA 2 is frequency doubled in SHG and split to generate the UV pump and probe beams. All three beams are co-incident on the sample, which is placed in the UHV system, with the TOF detector placed 3-5mm from the sample.

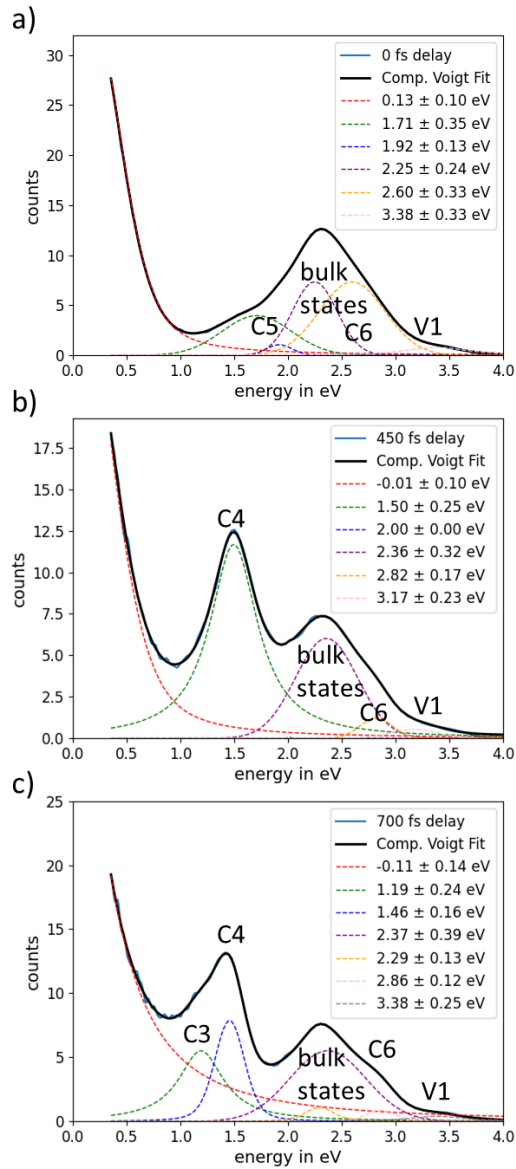


Fig. S5. Example composite Voigt fits of the P-rich InP(100) surface, at time delays of 0 fs (a), 450 fs (b) and 700 fs (c). Final state positions are determined by focusing on time delay slices at which the respective state is clearly visible, and averaging out kinetic energy values between slices. Re-printed from [33], with state labels added.

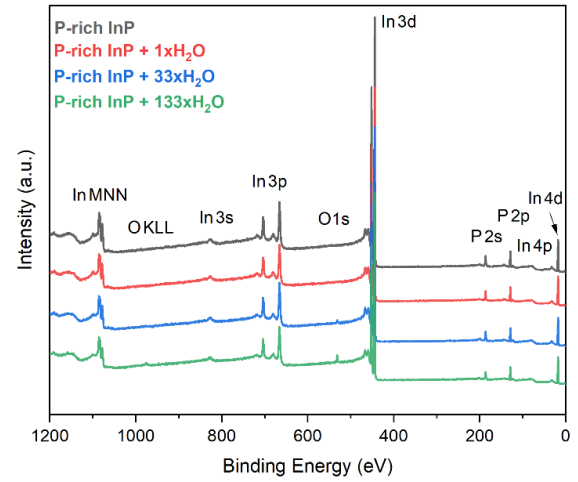


Fig. S6: XP spectra of the P-rich InP surface (grey), both prior to and after increasing numbers of the water exposure cycles (just H₂O). On the P-rich InP surface after a single cycle the O 1s state is not visible (red spectrum). At 33 and 133 cycles the O 1s state becomes visible, the peak related to the Auger O KLL follows the same pattern.

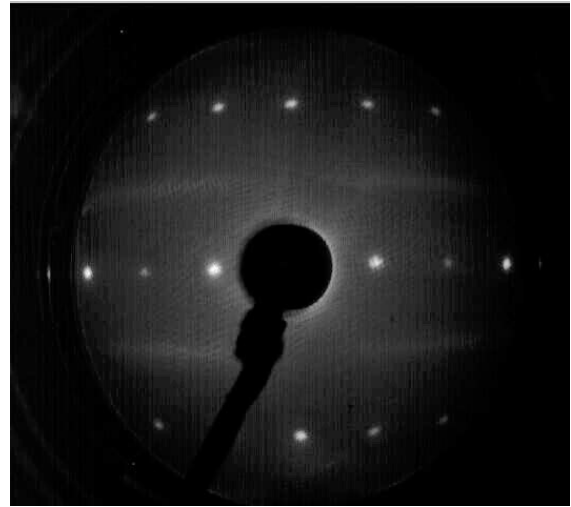


Fig. S7. The (2x1)-like LEED pattern of the P-rich InP surface after annealing at 200°C for 1 h.

Supplementary Note 1: Prior tr-2PPE studies of bare P-rich InP and under TiO₂ deposition

The present work builds upon a previous investigation of the bare P-rich InP(100) surface by the present authors, published in ref. [33], as well as a follow-up paper on TiO₂ deposition on this surface using ALD [35]. Key results relevant to the current study are summarized here:

The P-rich InP(100) surface, grown via MOVPE on p-doped InP, exhibits a $p(2 \times 2)/c(4 \times 2)$ surface reconstruction, characterized by P-dimers passivated by hydrogen atoms. Tr-2PPE measurements revealed a rich near-surface electronic landscape of at least nine distinct states located around the bandgap (Fig. 3a, Fig. S8) [33]. These include near-surface localized conduction band states C1 to C6, a near-surface bulk-to-surface transition cluster ("bulk state"), a mid-gap surface state that pins the Fermi level, and a valence band state V1. Through DFT calculations it was shown that C1, C2, and C4 are particularly prone to the migration of photoexcited electrons from bulk to the surface, in large part using the bulk-to-surface transition state as an intermediate step. This correlates well to the increased relative emission intensity of these states. The average decay of photoexcited electrons in the near-surface region is shown in Fig. S8, with electrons reaching the Fermi level in around 1.8 ± 0.2 ps.

The lowest energy conduction band state C1 was found to be located at the CBM, and strongly localized in the uppermost surface atomic layers. Other states such as C3 and C6 were found to be less surface localized. Surface states were shown to play a key role in carrier transport to the surface, whilst also contributing to near-surface recombination processes. The mix of near-surface and sub-surface states allows for their use as a sensitive probe of modifications to the top atomic layers. Sub-surface associated states and clusters of states are unlikely to change with modification of only the uppermost few atomic layers, whilst near-surface and surface states are likely to be more strongly affected. This was probed in ref [35] via TiO₂ deposition, further supporting C4, C2 and C1 as the main points where photoexcited electrons reach the surface. These states are thus particularly important for surface photo-electrochemistry, and their reactions *in operando* are thus potentially highly relevant to device performance. The present study uses this same P-rich surface as a model platform to examine how water exposure and subsequent formation of surface phosphates modulates the electronic structure and ultrafast dynamics of these near-surface states. Readers are referred to ref. [33] for more detailed spectroscopic and temporal dynamics data and discussions.

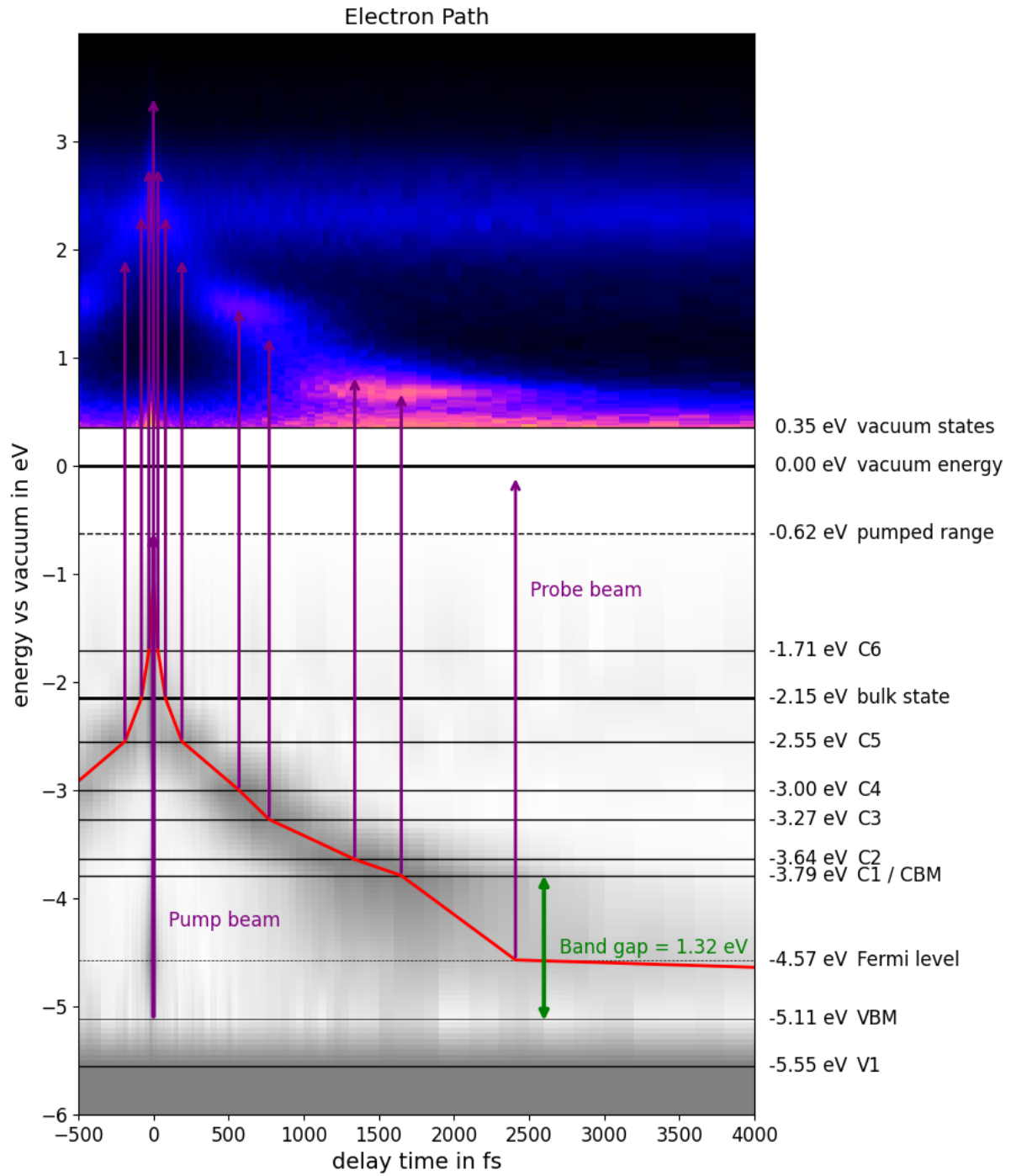


Fig. S8: Schematic of the InP(100) near-surface states relative to vacuum level, and their associated tr-2PPE emissions. The decay path of an average photoexcited electron is given in red, with the band gap denoted in green. The grey shading below vacuum energy are reconstructed from the tr-2PPE data, and represent the densities of photoexcited electrons at the respective energies and pump-probe delay times. Image re-printed from [33]

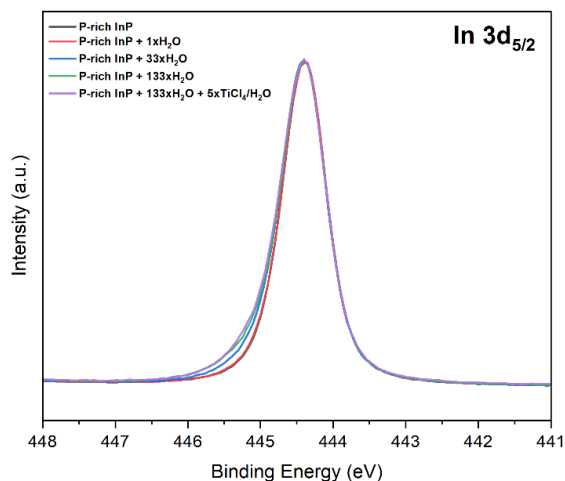


Fig. S9: XPS fine spectra of In 3d_{5/2} showing the increasing asymmetry at the higher binding energy from 33 cycles of water exposure due to the formation of indium phosphate compounds.

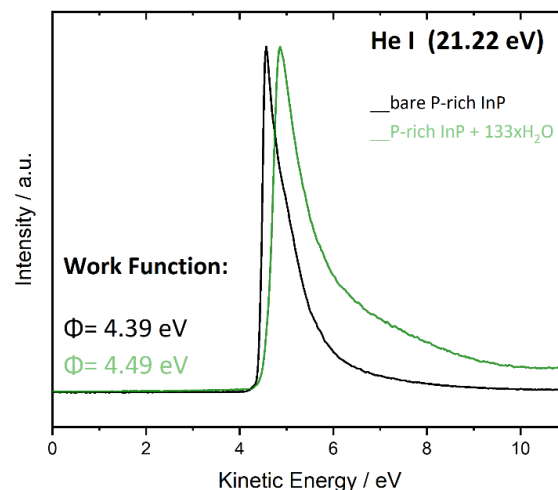


Fig. S11: The lower edge of emission in He I UPS is shown for the pure P-rich InP surface as well as after 133 cycles of water exposure. The work functions are determined at the half-maximum of the lower edge of emission.

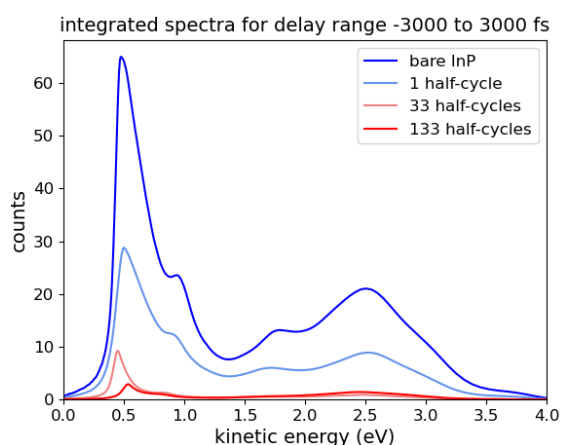


Fig. S10: Emission from -3000 to +3000 fs is integrated for the bare P-rich InP surface, as well as after water exposure, data corresponding to Fig. 3. There is a clearly observable decline in overall emission amplitude with increasing water exposure across the kinetic energy range.

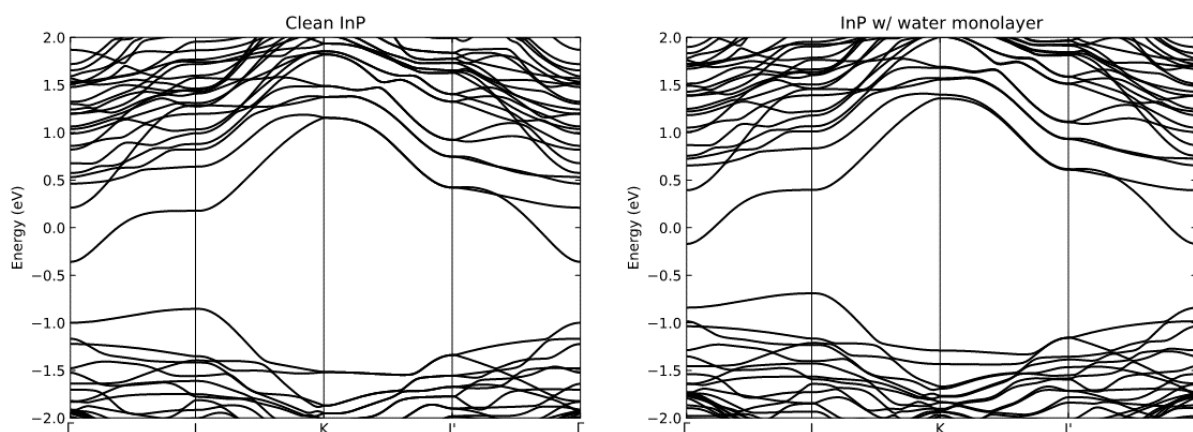


Fig. S12: DFT band diagrams for the pure P-rich InP surface (left) and after water exposure (right), showing little change in the near-gap region.

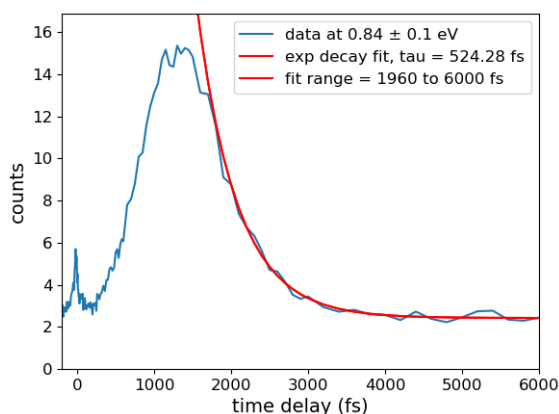


Fig. S13: Example exponential decay constant fit for C2 on the bare P-rich InP surface, data from Fig. 4a. Data is fitted from the half-maximum in the decay flank of emission, which is at 1960 fs in this example. Lower delay times are ignored to fit only the near-exponential component of decay, and avoid inaccuracies due to the emission peak (at around 1200 fs in this example).

Supplementary Note 2: Water modified electron dynamics from density functional theory

To gain a deeper understanding of the electron dynamics at the optically excited InP surface, density-functional theory (DFT) calculations are performed. The P-rich InP surface is modelled using the (2×2) -2D-2H structure, corresponding to the $p(2 \times 2)/c(2 \times 4)$ reconstruction⁴⁶. The computational details correspond to the previous calculations reported in Ref.¹⁷. Both the clean surface as well as water-covered structures were considered. To more accurately capture the experimental impact of water exposure, we modeled surface adsorption for both a single water monomer and a monolayer of water.

Single water monomers preferably adsorb in the trench between the P dimer rows¹⁷. We mention that in addition to this structure, another, even more favorable anchor points exists that may help to stabilize water overlayers on the InP surface: An increase of the water adsorption energy from 0.21 to 0.36 eV is calculated for water molecules that bond to pre-adsorbed hydroxyl groups attached to P dimers (Fig. S14). This may help stabilize the adsorbed water molecules from desorption in UHV (such as during tr-2PPE measurements in UHV), or during ongoing chemical reactions *in situ*. These binding energies exceed $k_B T$ both at room temperature and 200 °C by about an order of magnitude, thus ensuring water desorption rates are slowed sufficiently for measurements of the water-adsorbed surface to be possible. The water monolayer covered surface was modelled with a hydrogen-bonded network of 9 molecules attached to the surface within a (2×2) unit cell. Remarkably, the atomic geometry of the InP (100) surface as well as the orbital character and energy as well as dispersion of the InP surface states is not strongly affected by the water adsorption, see Fig. S11. This confirms previous findings¹⁷.

Constrained DFT^{59–61} is used to determine excited-state potential-energy surfaces (PES). Ab initio molecular dynamics (AIMD) calculations on the excited-state potential-energy surfaces (PES)^{62,63} are used to determine the time evolution of the excited states. Transitions between the excited-state PES are modelled using Tully's surface hopping algorithm⁶⁴ as implemented in the Libra-X program package⁶⁵. Starting point of the AIMD is an optically excited state where an electron from the highest valence surface state has been excited into the lowest surface conduction state C1, cf. Ref.¹⁹. C1 is the focus of the calculations due to the strong experimentally observed effects of water exposure on the lifetimes of this state (Fig. 4). Fifty room temperature

trajectories are calculated for clean InP surfaces as well as for single water monomer and water monolayer adsorbed surfaces. Transitions from C1 across the band gap to the highest valence surface state, as well as energetically upwards to C2 are allowed for in these trajectories.

Upon analyzing these trajectories, it is observed that in some cases electronic transitions occur within a few femtoseconds, while in others, there are no changes in the occupation numbers within the full simulation time of 180 fs. Remarkably, all trajectories where PES transitions occur are characterized by rapid movements and large displacement of the uppermost P atoms. This is in line with the localization of the surface states involved in the calculations: all three surface states are P-dimer localized¹⁹. Thus, P-dimer related surface vibrations are expected to induce electronic transitions involving these states. While, on the one hand, the occupation number dynamics is strongly correlated with surface atom dynamics, we find, on the other hand, a strong correlation between the surface structural dynamics and the water coverage. This can be seen in Fig. S13, where we average the surface atom displacement from the equilibrium positions for 50 trajectories calculated for clean, monomer, and monolayer-covered surfaces, respectively. Clearly, the water overlayer dampens the surface vibrations. In particular, we observe a damping of the vertical displacements of the P atoms along with a reduced magnitude of the P dimer stretching vibrations. At the same time, Fig. 5 shows a clear dependence of the lifetime of the excited electron occupying C1 on the water coverage: The higher the water coverage, the longer the lifetime. Given that the water adsorption essentially neither modifies the surface atomic structure nor the surface electronic states of the InP surface, but strongly affects its dynamics, we conclude that the dampening of the InP surface vibrations of the corresponding surface phonon modes is instrumental for the experimentally observed lifetime prolongation. This effect can be understood from the vibration induced transitory increase in wave function overlap, and thus increase in hopping probability between the involved surface state. The present observation agrees with previous theoretical modeling of the transfer dynamics of photogenerated electrons on In-rich InP surfaces^{19,66} as well as with similar observations that were recently made for water-adsorbed⁶⁷ as well as doped titania⁶⁸. Such extension of lifetimes may make these states significantly more relevant to chemical reactions at the surface than indicated by comparing their UHV lifetimes to the reaction rates at the surface.

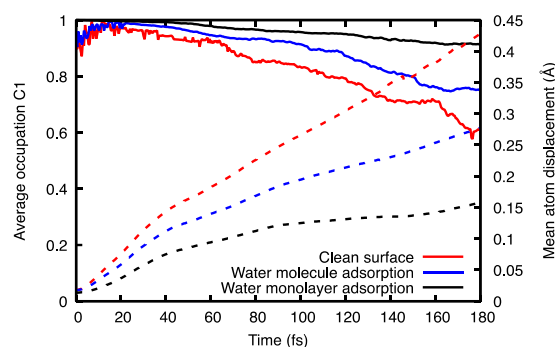


Fig. S14: Average time dependence of the C1 occupation (solid line) and the P-rich InP(100) surface atoms displacement from the equilibrium positions (dashed line) as calculated from AIMD.

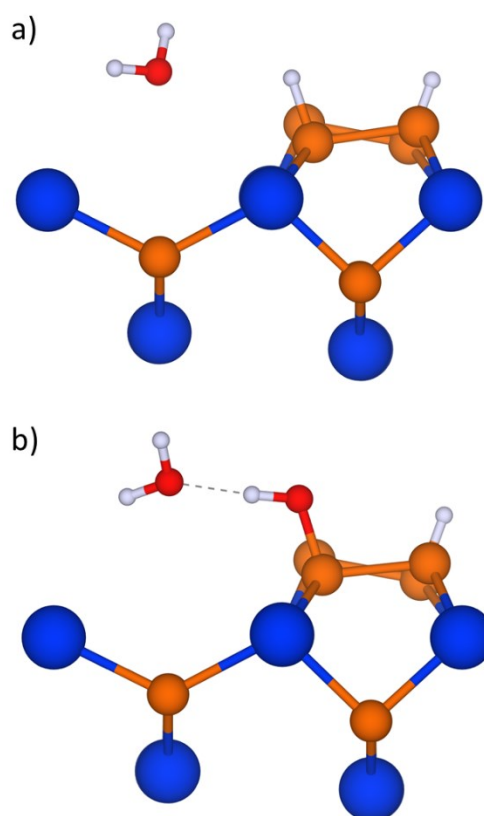


Fig. S15: Single water monomers preferentially adsorb in the valley between P-dimer rows as shown in (a) at a binding energy of 0.21 eV. They can be further stabilized by bonding to pre-adsorbed OH-groups (b), increasing the binding energy to 0.36 eV. We theorize that this stabilizes the adsorbed H₂O molecules under UHV exposure for tr-2PPE measurements.

REFERENCES

- (1) Cheng, W.-H.; Richter, M. H.; May, M. M.; Ohlmann, J.; Lackner, D.; Dimroth, F.; Hannappel, T.; Atwater, H. A.; Lewerenz, H.-J. Monolithic Photoelectrochemical Device for Direct Water Splitting with 19% Efficiency. *ACS Energy Lett.* **2018**, *3* (8), 1795–1800. <https://doi.org/10.1021/acsenergylett.8b00920>.
- (2) Yin, X.; Battaglia, C.; Lin, Y.; Chen, K.; Hettick, M.; Zheng, M.; Chen, C.-Y.; Kiriya, D.; Javey, A. 19.2% Efficient InP Heterojunction Solar Cell with Electron-Selective TiO₂(2) Contact. *ACS Photonics* **2014**, *1* (12), 1245–1250. <https://doi.org/10.1021/ph500153c>.
- (3) Gao, L.; Cui, Y.; Vervuurt, R. H. J.; van Dam, D.; van Veldhoven, R. P. J.; Hofmann, J. P.; Bol, A. A.; Haverkort, J. E. M.; Notten, P. H. L.; Bakkers, E. P. A. M.; Hensen, E. J. M. Photoelectrodes: High-Efficiency InP-Based Photocathode for Hydrogen Production by Interface Energetics Design and Photon Management (Adv. Funct. Mater. 5/2016). *Adv. Funct. Mater.* **2016**, *26* (5), 633–633. <https://doi.org/10.1002/adfm.201670028>.
- (4) Lee, M. H.; Takei, K.; Zhang, J.; Kapadia, R.; Zheng, M.; Chen, Y.-Z.; Nah, J.; Matthews, T. S.; Chueh, Y.-L.; Ager, J. W.; Javey, A. P-Type InP Nanopillar Photocathodes for Efficient Solar-Driven Hydrogen Production. *Angew. Chem. Int. Ed.* **2012**, *51* (43), 10760–10764. <https://doi.org/10.1002/anie.201203174>.
- (5) Muñoz, A. G.; Heine, C.; Lublow, M.; Klemm, H. W.; Szabó, N.; Hannappel, T.; Lewerenz, H.-J. Photoelectrochemical Conditioning of MOVPE P-InP Films for Light-Induced Hydrogen Evolution: Chemical, Electronic and Optical Properties. *ECS J. Solid State Sci. Technol.* **2013**, *2* (4), Q51. <https://doi.org/10.1149/2.016304jss>.
- (6) Aspnes, D. E.; Studna, A. A. Dielectric Functions and Optical Parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV. *Phys Rev B* **1983**, *27* (2), 985–1009. <https://doi.org/10.1103/PhysRevB.27.985>.
- (7) Wang, J.; Sciarrino, F.; Laing, A.; Thompson, M. G. Integrated Photonic Quantum Technologies. *Nat. Photonics* **2020**, *14* (5), 273–284. <https://doi.org/10.1038/s41566-019-0532-1>.
- (8) Smit, M.; Williams, K.; van der Tol, J. Past, Present, and Future of InP-Based Photonic Integration. *APL Photonics* **2019**, *4* (5), 050901. <https://doi.org/10.1063/1.5087862>.
- (9) Wang, Y.; Jiao, Y.; Williams, K. Scaling Photonic Integrated Circuits with InP Technology: A Perspective. *APL Photonics* **2024**, *9* (5), 050902. <https://doi.org/10.1063/5.0200861>.
- (10) Li, L.; Han, B.-K.; Fu, Q.; Hicks, R. F. Example of a Compound Semiconductor Surface That Mimics Silicon: The InP(001)-(2×1) Reconstruction. *Phys. Rev. Lett.* **1999**, *82* (9), 1879–1882. <https://doi.org/10.1103/physrevlett.82.1879>.
- (11) Wood, B. C.; Schwegler, E.; Choi, W. I.; Ogitsu, T. Surface Chemistry of GaP(001) and InP(001) in Contact with Water. *J. Phys. Chem. C* **2014**, *118* (2), 1062–1070. <https://doi.org/10.1021/jp4098843>.
- (12) May, M. M.; Supplie, O.; Hóhn, C.; van de Krol, R.; Lewerenz, H.-J.; Hannappel, T. The Interface of GaP(100) and H₂O Studied by Photoemission and Reflection Anisotropy Spectroscopy. *New J Phys* **2013**, *15*, 103003.
- (13) Kleinschmidt, P.; Döscher, H.; Vogt, P.; Hannappel, T. Direct Observation of Dimer Flipping at the Hydrogen-Stabilized GaP(100) and InP(100) Surfaces. *Phys Rev B* **2011**, *83* (15), 155316. <https://doi.org/10.1103/PhysRevB.83.155316>.
- (14) Muñoz, A. G.; Heine, C.; Klemm, H. W.; Hannappel, T.; Szabo, N.; Lewerenz, H.-J. Electrochemical Passivation of Homoepitaxial InP (100) Thin Films for Light Induced Hydrogen Evolution: A Synchrotron Radiation Photoelectron Spectroscopy Study. *ECS Trans.* **2011**, *35* (8), 141–150. <https://doi.org/10.1149/1.3567746>.
- (15) Lin, Y.; Kapadia, R.; Yang, J.; Zheng, M.; Chen, K.; Hettick, M.; Yin, X.; Battaglia, C.; Sharp, I. D.; Ager, J. W.; Javey, A. Role of TiO₂ Surface Passivation on Improving the Performance of P-InP Photocathodes. *J. Phys. Chem. C* **2015**, *119* (5), 2308–2313. <https://doi.org/10.1021/jp5107313>.
- (16) Aharon-Shalom, E.; Heller, A. Efficient p - InP (Rh - H Alloy) and p - InP (Re - H Alloy) Hydrogen Evolving Photocathodes. *J. Electrochem. Soc.* **1982**, *129* (12), 2865–2866. <https://doi.org/10.1149/1.2123695>.
- (17) Moritz, D. C.; Ruiz Alvarado, I. A.; Zare Pour, M. A.; Paszuk, A.; Frieß, T.; Runge, E.; Hofmann, J. P.; Hannappel, T.; Schmidt, W. G.; Jaegermann, W. P-Terminated InP (001) Surfaces: Surface Band Bending and Reactivity to Water. *ACS Appl. Mater. Interfaces* **2022**, *14* (41), 47255–47261. <https://doi.org/10.1021/acsaami.2c13352>.
- (18) May, M. M.; Lewerenz, H.-J.; Hannappel, T. Optical in Situ Study of InP(100) Surface Chemistry: Dissociative Adsorption of Water and Oxygen. *J. Phys. Chem. C* **2014**, *118* (33), 19032–19041. <https://doi.org/10.1021/jp502955m>.
- (19) Sciotto, R.; Ruiz Alvarado, I. A.; Schmidt, W. G. Substrate Doping and Defect Influence on P-Rich InP(001):H Surface Properties. *Surfaces* **2024**, *7* (1), 79–87. <https://doi.org/10.3390/surfaces7010006>.
- (20) Löw, M.; Guidat, M.; Kim, J.; May, M. M. The Interfacial Structure of InP(100) in Contact with

- HCl and H₂SO₄ Studied by Reflection Anisotropy Spectroscopy. *RSC Adv.* **2022**, *12* (50), 32756–32764. <https://doi.org/10.1039/d2ra05159a>.
- (21) Xu, Z.; Hou, B.; Zhao, F.; Cai, Z.; Shi, H.; Liu, Y.; Hill, C. L.; Musaev, D. G.; Mecklenburg, M.; Cronin, S. B.; Lian, T. Nanoscale TiO₂ Protection Layer Enhances the Built-In Field and Charge Separation Performance of GaP Photoelectrodes. *Nano Lett.* **2021**, *21* (19), 8017–8024. <https://doi.org/10.1021/acs.nanolett.1c02257>.
- (22) Young, J. L.; Steiner, M. A.; Döschner, H.; France, R. M.; Turner, J. A.; Deutsch, T. G. Direct Solar-to-Hydrogen Conversion via Inverted Metamorphic Multi-Junction Semiconductor Architectures. *Nat. Energy* **2017**, *2* (4). <https://doi.org/10.1038/nenergy.2017.28>.
- (23) Heller, A.; Vadimsky, R. G. Efficient Solar to Chemical Conversion: 12% Efficient Photoassisted Electrolysis in the [p-Type InP(Ru)]/HCl-KCl/Pt(Rh) Cell. *Phys Rev Lett* **1981**, *46* (17), 1153. <https://doi.org/10.1103/physrevlett.46.1153>.
- (24) Hu, S.; Shaner, M. R.; Beardslee, J. A.; Lichterman, M.; Brunschwig, B. S.; Lewis, N. S. Amorphous TiO₂ Coatings Stabilize Si, GaAs, and GaP Photoanodes for Efficient Water Oxidation. *Science* **2014**, *344* (6187), 1005–1009. <https://doi.org/10.1126/science.1251428>.
- (25) Bae, D.; Shayestehaminzadeh, S.; Thorsteinsson, E. B.; Pedersen, T.; Hansen, O.; Seger, B.; Vesborg, P. C. K.; Ólafsson, S.; Chorkendorff, I. Protection of Si Photocathode Using TiO₂ Deposited by High Power Impulse Magnetron Sputtering for H₂ Evolution in Alkaline Media. *Sol. Energy Mater. Sol. Cells* **2016**, *144*, 758–765. <https://doi.org/10.1016/j.solmat.2015.10.020>.
- (26) Seger, B.; Pedersen, T.; Laursen, A. B.; Vesborg, P. C. K.; Hansen, O.; Chorkendorff, I. Using TiO₂ as a Conductive Protective Layer for Photocathodic H₂ Evolution. *J. Am. Chem. Soc.* **2013**, *135* (3), 1057–1064. <https://doi.org/10.1021/ja309523t>.
- (27) Mei, B.; Pedersen, T.; Malacrida, P.; Bae, D.; Frydendal, R.; Hansen, O.; Vesborg, P. C. K.; Seger, B.; Chorkendorff, I. Crystalline TiO₂: A Generic and Effective Electron-Conducting Protection Layer for Photoanodes and -Cathodes. *J. Phys. Chem. C* **2015**, *119* (27), 15019–15027. <https://doi.org/10.1021/acs.jpcc.5b04407>.
- (28) Abendroth, B.; Moebus, T.; Rentrop, S.; Strohmeyer, R.; Vinnichenko, M.; Weling, T.; Stöcker, H.; Meyer, D. C. Atomic Layer Deposition of TiO₂ from Tetrakis(Dimethylamino)Titanium and H₂O. *Thin Solid Films* **2013**, *545*, 176–182. <https://doi.org/10.1016/j.tsf.2013.07.076>.
- (29) Kaufman, A. J.; Krivina, R. A.; Shen, M.; Boettcher, S. W. Controlling Catalyst–Semiconductor Contacts: Interfacial Charge Separation in p-InP Photocathodes. *ACS Energy Lett.* **2022**, *7* (1), 541–549. <https://doi.org/10.1021/acscenergylett.1c02590>.
- (30) Gu, J.; Yan, Y.; Young, J. L.; Steirer, K. X.; Neale, N. R.; Turner, J. A. Water Reduction by a P-GaInP₂ Photoelectrode Stabilized by an Amorphous TiO₂ Coating and a Molecular Cobalt Catalyst. *Nat. Mater.* **2015**, *15* (4), 456–460. <https://doi.org/10.1038/nmat4511>.
- (31) Moehl, T.; Suh, J.; Sévery, L.; Wick-Joliat, R.; Tilley, S. D. Investigation of (Leaky) ALD TiO₂ Protection Layers for Water-Splitting Photoelectrodes. *ACS Appl. Mater. Interfaces* **2017**, *9* (50), 43614–43622. <https://doi.org/10.1021/acscami.7b12564>.
- (32) J. van Engelen; S. Reniers; J. Bolk; K. Williams; J. van der Tol; Y. Jiao. Low Loss InP Membrane Photonic Integrated Circuits Enabled by 193-Nm Deep UV Lithography. In *2019 Compound Semiconductor Week (CSW)*; 2019; pp 1–2. <https://doi.org/10.1109/ICIPRM.2019.8819069>.
- (33) Diederich, J.; Velasquez Rojas, J.; Zare Pour, M. A.; Ruiz Alvarado, I. A.; Paszuk, A.; Sciotto, R.; Höhn, C.; Schwarzburg, K.; Ostheimer, D.; Eichberger, R.; Schmidt, W. G.; Hannappel, T.; van de Krol, R.; Friedrich, D. Unraveling Electron Dynamics in P-Type Indium Phosphide (100): A Time-Resolved Two-Photon Photoemission Study. *J. Am. Chem. Soc.* **2024**, *146* (13), 8949–8960. <https://doi.org/10.1021/jacs.3c12487>.
- (34) Johnson, R. W.; Hultqvist, A.; Bent, S. F. A Brief Review of Atomic Layer Deposition: From Fundamentals to Applications. *Mater. Today* **2014**, *17* (5), 236–246. <https://doi.org/10.1016/j.mattod.2014.04.026>.
- (35) Diederich, J.; Rojas, J. V.; Paszuk, A.; Pour, M. A. Z.; Höhn, C.; Alvarado, I. A. R.; Schwarzburg, K.; Ostheimer, D.; Eichberger, R.; Schmidt, W. G.; Hannappel, T.; van de Krol, R.; Friedrich, D. Ultrafast Electron Dynamics at the P-Rich Indium Phosphide/TiO₂ Interface. *Adv. Funct. Mater.* **2024**, *34* (49), 2409455. <https://doi.org/10.1002/adfm.202409455>.
- (36) Cen, J.; Wu, Q.; Liu, M.; Orlov, A. Developing New Understanding of Photoelectrochemical Water Splitting via In-Situ Techniques: A Review on Recent Progress. *Spec. Issue New Energy Catal.* **2017**, *2* (2), 100–111. <https://doi.org/10.1016/j.gee.2017.03.001>.
- (37) Töben, L.; Hannappel, T.; Eichberger, R.; Möller, K.; Gundlach, L.; Ernstorfer, R.; Willig, F. Two-Photon Photoemission as a Probe of

- Unoccupied and Occupied Surface States of InP(100). *J. Cryst. Growth* **2003**, *248*, 206–210. [https://doi.org/10.1016/s0022-0248\(02\)01884-5](https://doi.org/10.1016/s0022-0248(02)01884-5).
- (38) Ueba, H.; Gumhalter, B. Theory of Two-Photon Photoemission Spectroscopy of Surfaces. *Dyn. Electron Transf. Process. Surf.* **2007**, *82* (4), 193–223. <https://doi.org/10.1016/j.progsurf.2007.03.002>.
- (39) Borgwardt, M.; Omelchenko, S. T.; Favaro, M.; Plate, P.; Höhn, C.; Abou-Ras, D.; Schwarzburg, K.; van de Krol, R.; Atwater, H. A.; Lewis, N. S.; Eichberger, R.; Friedrich, D. Femtosecond Time-Resolved Two-Photon Photoemission Studies of Ultrafast Carrier Relaxation in Cu₂O Photoelectrodes. *Nat. Commun.* **2019**, *10* (1), 2106. <https://doi.org/10.1038/s41467-019-10143-x>.
- (40) Sherwood, P. M. A. Rapid Evaluation of the Voigt Function and Its Use for Interpreting X-Ray Photoelectron Spectroscopic Data. *Surf. Interface Anal.* **2019**, *51* (2), 254–274. <https://doi.org/10.1002/sia.6577>.
- (41) Petek, H.; Ogawa, S. Femtosecond Time-Resolved Two-Photon Photoemission Studies of Electron Dynamics in Metals. *Prog. Surf. Sci.* **1997**, *56* (4), 239–310. [https://doi.org/10.1016/s0079-6816\(98\)00002-1](https://doi.org/10.1016/s0079-6816(98)00002-1).
- (42) Chen, G.; Visbeck, S. B.; Law, D. C.; Hicks, R. F. Structure-Sensitive Oxidation of the Indium Phosphide (001) Surface. *J Appl Phys* **2002**, *91*, 9362. <https://doi.org/10.1063/1.1471577>.
- (43) Lewerenz, H. J.; Schulte, K. H. Combined Photoelectrochemical Conditioning and Surface Analysis of InP Photocathodes: II. Photoelectron Spectroscopy. *Electrochim Acta* **2002**, *47*, 2639.
- (44) Alvarado Ruiz, I. A.; Schmidt, W. G. Water/InP(001) from Density Functional Theory. *ACS Omega* **2022**, *7*, 19355.
- (45) Vogt, P.; Frisch, A. M.; Hannappel, Th.; Visbeck, S.; Willig, F.; Jung, Ch.; Follath, R.; Braun, W.; Richter, W.; Esser, N. Atomic Structure and Composition of the P-Rich InP(001) Surfaces. *Appl. Surf. Sci.* **2000**, *166* (1–4), 190–195. [https://doi.org/10.1016/s0169-4332\(00\)00411-6](https://doi.org/10.1016/s0169-4332(00)00411-6).
- (46) Schmidt, W. G.; Hahn, P. H.; Bechstedt, F.; Esser, N.; Vogt, P.; Wange, A.; Richter, W. InP(001)-(2×1) Surface: A Hydrogen Stabilized Structure. *Phys. Rev. Lett.* **2003**, *90* (12), 126101. <https://doi.org/10.1103/physrevlett.90.126101>.
- (47) Goryachev, A.; Gao, L.; van Veldhoven, R. P. J.; Haverkort, J. E. M.; Hofmann, J. P.; Hensen, E. J. M. On the Origin of the Photocurrent of Electrochemically Passivated P-InP(100) Photoelectrodes. *Phys Chem Chem Phys* **2018**, *20* (20), 14242–14250. <https://doi.org/10.1039/C8CP00894A>.
- (48) Hannappel, T.; Töben, L.; Möller, K.; Willig, F. In-Situ Monitoring of InP(100) and GaP(100) Interfaces and Characterization with RDS at 20 K. *J. Electron. Mater.* **2001**, *30* (11), 1425–1428. <https://doi.org/10.1007/s11664-001-0196-7>.
- (49) Hollinger, G.; Bergignat, E.; Joseph, J.; Robach, Y. On the Nature of Oxides on InP Surfaces. *J Vac Sci Technol A* **1985**, *3* (6), 2082.
- (50) Zhang, X.; Pham, T. A.; Ogitsu, T.; Wood, B. C.; Ptasinska, S. Modulation of Surface Bonding Topology: Oxygen Bridges on OH-Terminated InP (001). *J. Phys. Chem. C* **2020**, *124* (5), 3196–3203. <https://doi.org/10.1021/acs.jpcc.9b11548>.
- (51) Henderson, M. A. The Interaction of Water with Solid Surfaces: Fundamental Aspects Revisited. *ChemInform* **2002**, *33* (47), 228–228. <https://doi.org/10.1002/chin.200247228>.
- (52) May, M. M.; Supplie, O.; Höhn, C.; Zabka, W.-D.; Lewerenz, H.-J.; van de Krol, R.; Hannappel, T. Water-Induced Modifications of GaP(100) and InP(100) Surfaces Studied by Photoelectron Spectroscopy and Reflection Anisotropy Spectroscopy. *Sol. Hydrog. Nanotechnol. VIII* **2013**, *46*, 8822, 88220M (pp. 1–7). <https://doi.org/10.1117/12.2026172>.
- (53) Hannappel, T.; Visbeck, S.; Knorr, K.; Mahrt, J.; Zorn, M.; Willig, F. Preparation of P-Rich InP Surfaces via MOCVD and Surface Characterization in UHV. *Appl. Phys. A* **1999**, *69* (4), 427–431. <https://doi.org/10.1007/s003390051026>.
- (54) Chen, G.; Cheng, S. F.; Tobin, D.; Li, L.; Raghavachari, K.; Hicks, R. F. Indium Phosphide (001)-(2×1): Direct Evidence for a Hydrogen-Stabilized Surface Reconstruction. *Phys. Rev. B* **2003**, *68* 8, 121303(R). <https://doi.org/10.1103/PhysRevB.68.121303>.
- (55) Faur, M.; Faur, M.; Jayne, D. T.; Goradia, M.; Goradia, C. XPS Investigation of Anodic Oxides Grown on P-Type InP. *Surf Interface Anal* **1990**, *15* (11), 641.
- (56) Petit, E. J.; Houzay, F.; Moison, J. M. Interaction of Atomic Hydrogen with Native Oxides on InP(100). *Surf. Sci.* **1992**, *269–270*, 902–908. [https://doi.org/10.1016/0039-6028\(92\)91367-K](https://doi.org/10.1016/0039-6028(92)91367-K).
- (57) Stietz, F.; Woll, J.; Persch, V.; Allinger, T.; Erfurth, W.; Goldmann, A. M.; Schaefer, J. A. Interaction of Hydrogen and Methane with Inp100) and GaAs(100) Surfaces. *Phys. Status Solidi A* **1997**, *159*, 185–194. [https://doi.org/10.1002/1521-396X\(199701\)159:1<185::AID-PSSA185>3.0.CO;2-M](https://doi.org/10.1002/1521-396X(199701)159:1<185::AID-PSSA185>3.0.CO;2-M).
- (58) Sippel, P. Electronic Structure and Electron Dynamics in Semiconductor Materials for New

- Photovoltaic Applications , Ph.D. Thesis, Technische Universität Ilmenau, Ilmenau, Germany **2015**. Available online: https://www.db-thueringen.de/servlets/MCRFileNodeServlet/dtbt_derivate_00032541/ilm1-2015000378.pdf. DOI: 10.2314/GBV:883883184.
- (59) Pankratov, O.; Scheffler, M. Localized Excitons and Breaking of Chemical Bonds at III-V (110) Surfaces. *Phys. Rev. Lett.* **1995**, *75* (4), 701–704. <https://doi.org/10.1103/physrevlett.75.701>.
- (60) Artacho, E.; Rohlffing, M.; Côté, M.; Haynes, P. D.; Needs, R. J.; Molteni, C. Structural Relaxations in Electronically Excited Poly(Para-Phenylene). *Phys. Rev. Lett.* **2004**, *93* (11), 116401. <https://doi.org/10.1103/physrevlett.93.116401>.
- (61) Tiago, M. L.; Ismail-Beigi, S.; Louie, S. G. Effect of Semicore Orbitals on the Electronic Band Gaps of Si, Ge, and GaAs within the GW Approximation. *Phys. Rev. B* **2004**, *69* (12), 125212. <https://doi.org/10.1103/physrevb.69.125212>.
- (62) Frigge, T.; Hafke, B.; Witte, T.; Krenzer, B.; Streubühr, C.; Samad Syed, A.; Mikšić Trontl, V.; Avigo, I.; Zhou, P.; Ligges, M.; von der Linde, D.; Bovensiepen, U.; Horn-von Hoegen, M.; Wippermann, S.; Lücke, A.; Sanna, S.; Gerstmann, U.; Schmidt, W. G. Optically Excited Structural Transition in Atomic Wires on Surfaces at the Quantum Limit. *Nature* **2017**, *544* (7649), 207–211. <https://doi.org/10.1038/nature21432>.
- (63) Nicholson, C. W.; Lücke, A.; Schmidt, W. G.; Puppig, M.; Rettig, L.; Ernstorfer, R.; Wolf, M. Beyond the Molecular Movie: Dynamics of Bands and Bonds during a Photoinduced Phase Transition. *Science* **2018**, *362* (6416), 821–825. <https://doi.org/10.1126/science.aar4183>.
- (64) Tully, J. C. Molecular Dynamics with Electronic Transitions. *J. Chem. Phys.* **1990**, *93* (2), 1061–1071. <https://doi.org/10.1063/1.459170>.
- (65) Pradhan, E.; Sato, K.; Akimov, A. V. Non-Adiabatic Molecular Dynamics with Δ SCF Excited States. *J. Phys. Condens. Matter* **2018**, *30* (48), 484002. <https://doi.org/10.1088/1361-648x/aae864>.
- (66) Glahn, L. J.; Ruiz Alvarado, I. A.; Neufeld, S.; Zare Pour, M. A.; Paszuk, A.; Ostheimer, D.; Shekarabi, S.; Romanyuk, O.; Moritz, D. C.; Hofmann, J. P.; Jaegermann, W.; Hannappel, T.; Schmidt, W. G. Clean and Hydrogen-Adsorbed AlInP(001) Surfaces: Structures and Electronic Properties. *Phys. Status Solidi B* **2022**, *259* (11), 2200308. <https://doi.org/10.1002/pssb.202200308>.
- (67) Xu, Z.-F.; Tong, C.-J.; Si, R.; Teobaldi, G.; Liu, L.-M. Nonadiabatic Dynamics of Polaron Hopping and Coupling with Water on Reduced TiO₂. *J. Phys. Chem. Lett.* **2022**, *13* (3), 857–863. <https://doi.org/10.1021/acs.jpclett.1c04231>.
- (68) Zhang, L.; Zheng, Q.; Xie, Y.; Lan, Z.; Prezhdo, O. V.; Saidi, W. A.; Zhao, J. Delocalized Impurity Phonon Induced Electron–Hole Recombination in Doped Semiconductors. *Nano Lett.* **2018**, *18* (3), 1592–1599. <https://doi.org/10.1021/acs.nanolett.7b03933>.