

Surface States for Photoelectrodes of Gallium Phosphide (GaP) with Surface-Specific Electronic Spectra and Phase Measurements

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Abstract Gallium phosphide (GaP) photoelectrodes have received tremendous attention owing to their applications in photocatalysis and the photoelectrocatalytic reduction of CO₂. Surface electronic states of GaP are important in such catalysis applications. However, knowledge of surface states of GaP under ambient conditions is lacking. Here we combined azimuth-dependent electronic sum frequency generation (ESFG) spectroscopy with phase measurements to investigate the surface states for *n*-type and *p*-type GaP(100) semiconductors. ESFG spectroscopic studies enabled us to identify three surface states of the GaP crystals under ambient conditions. These experiments have also shown that all the spectral features come from surface contributions for both the *n*-type and *p*-type GaP(100) crystals, and that both surface dipoles and surface charges were responsible for the electronic transitions of isotropic and anisotropic components. Combined with azimuth-dependent phase measurements, surface charges were found to account for the isotropic surface ESFG components: negative for the *n*-type, and positive for the *p*-type GaP(100). Finally, we conducted a thorough theoretical analysis of surface and bulk contributions for azimuth-dependent ESFG responses. With these spectral and phase signatures, we have further quantified surface and bulk contributions along different orientations for the *n*-type and *p*-type GaP(100) crystals.

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Introduction

Photocatalytic and photoelectrocatalytic reduction of CO₂ into valuable products has attracted more and more attention in recent years, promoting the reduction in fossil fuel use and possibly mitigating the greenhouse effect. In photocatalysis of CO₂, light is absorbed in the bandgap of photocatalysts to promote the CO₂ reaction at the surface.^{1, 2} For photoelectrocatalysis, higher CO₂ conversion rates are obtained by combining the photocatalytic and electrocatalytic CO₂ reduction processes.^{1, 3} In both photocatalysis and photoelectrocatalysis, semiconductors often act as photocathodes for the reduction of CO₂.⁴⁻¹³ Of these, *p*-type GaP has attracted tremendous attention due to its low-cost and high efficiency.^{10, 14-19} As a photoelectrode material, amorphous GaP is easily deposited under low temperatures as well as on varied substrates of plastic, glass and metal. In addition, GaP is one of a few materials which have both large solar light absorption and ideal band-edge positions for water splitting.²⁰⁻²² These attributes arise from GaP having a band gap of 2.26 eV^{20, 23, 24} and band edges which are above the hydrogen reduction potential.²² Recently, GaP photoelectrode materials have been applied in photocatalytic and photoelectrocatalytic CO₂ reduction.^{11, 25, 26} In the process of CO₂ reduction, GaP surfaces are always modified by other materials to make them photochemically more stable and improve the electronic conductivity,^{25, 27} but the question remains: what mechanisms are behind this improved performance? Theoretically, the mechanisms for the reaction on GaP photoelectrodes have been documented.^{23, 28} For example, Carter and co-workers discovered two pathways for photoelectrochemical CO₂ reduction on Ga-rich GaP(001) surface by using atomic-scale models based on density functional theory.²⁸ One such modeled mechanism is through a proton-coupled electron transfer pathway and the other by a hydride transfer pathway. While GaP surface structures, particularly surface states, influence the performance of photoelectrocatalytic CO₂ reduction processes, the surface roles of GaP in catalytic applications are experimentally unclear.

In previous studies, many surface non-specific tools such as Raman scattering²⁹, infrared and Raman spectroscopies,³⁰ cross-sectional transmission electron microscopy,³¹ ultraviolet photoelectron spectroscopy,³² minority-carrier capture,³³ time-resolved microwave conductivity,³⁴ photoemission spectroscopy,³⁵ and pump-probe spectroscopy³⁶ were utilized to study GaP surfaces. To some extent, these methods could provide some information of GaP surfaces. Nonetheless, much critical surface information may have been lost with such non-surface sensitive tools. In particular, surface states and their dynamics for semiconductors are lacking. Surface photovoltage spectroscopy³⁷⁻⁴¹ is often used to provide spectral information regarding subgap transitions of semiconductors in the space charge region (SCR). However, these SCR measurements are at most related to surface regions with tens of nanometers. Ultraviolet photoelectron spectroscopy,³² inverse photoemission,⁴² and two-photon photoemission⁴³⁻⁴⁵ were also used to investigate the surface states, but they must be performed under high vacuum.

In a free GaP surface, surface reconstructions and reactions with doping in the atmosphere produce electronic states, which lead to different energy positions from the other energy positions in the band structure, so called surface states.^{46, 47} Surface states are located inside the bandgap of the semiconductor and serve as localized free carrier traps. Depending on trapped charges, surface states are divided into two types: the positively charged donor-type and the negatively-charged acceptor-type.⁴⁸⁻⁵⁰ In the case of *n*-type GaP surfaces, the energy levels of acceptor-type surface states are located below its surface Fermi level, leading to the capture of electrons due to the flat-band condition.^{46, 47} On the other hand, the *n*-type GaP bulk must balance the surface negative charges via the conservation of the charge neutrality condition, resulting in an upward band bending for ionized donors in the depletion layer. For *p*-type GaP surfaces, the charge transfer between donor-type surface states and shallow acceptors leads to a downward band bending for the ionized acceptors. Since photoelectrochemical reactions of GaP photoelectrodes in solution occur under ambient conditions,^{10, 11, 14-22, 25} understanding these surfaces under such conditions is critical to their photocatalytic application.

Second-order nonlinear optical spectroscopic techniques, such as sum frequency generation (SFG) and second harmonic generation (SHG), have been widely used to investigate surfaces and interfaces due to their intrinsic surface specificity.⁵¹⁻⁶⁷ The advantage of SFG and SHG over other surface-sensitive methods is that they can be performed under any conditions for buried interfaces. As a surface/interface-specific tool, SFG can provide both electronic and vibrational properties, so called ESFG,⁶⁸⁻⁷⁸ and VSFG^{55, 57-64, 66, 67, 73, 79-93}, separately. Previous SHG intensity experiments extracted surface symmetries of semiconductors with azimuth-dependent measurements and displayed that the surface contribution was small in the semiconductor surfaces.⁹⁴⁻¹⁰¹ Electric field induced SHG methods have also been used to investigate semiconductor surfaces.^{94, 102-104} Vibrational SFG was recently used to study surface symmetry and contributions of GaAs(001) without spectral information.¹⁰⁵

Early SHG experiments utilized tunable lasers to acquire surface electronic spectra with point-by-point measurements, namely tunable SHG experiments.¹⁰⁶⁻¹⁰⁹ Other tunable SHG studies of semiconductors demonstrated excitonic transitions and resonant surface bands.¹¹⁰⁻¹¹⁴ These methods were hardly transferrable and were too inefficient for photoelectrochemical applications of GaP surfaces. However, current ESFG experiments have witnessed significant technological advances in broadband laser sources, greatly extending its breadth of application.^{70, 72-74, 76} In this work, we combined broadband ESFG spectra and phase measurement with azimuth-dependent experiments to study surface states and structural properties of both *n*-type and *p*-type GaP(100). Our goal was to identify the electronic transitions of the GaP surfaces and to uncover the nature of these transitions.

Theoretical Considerations

Before introducing the theory of ESFG, we shall begin with the symmetry of GaP(100). GaP(100) exhibits a zinc blende structure $\bar{4}3m (T_d)$, as depicted in Fig. 1(A). In the bulk, GaP possesses no birefringence and thereby orientation does not change light propagation. The top view of the GaP(100) surface is shown in the inset of Fig. 1(A). A bulk crystal coordinate system (a, b, c) is defined for the symmetry of GaP(100) bulk in Fig. 1(B), where the a, b , and c axes correspond to the principal axes of the crystal, $[100]$, $[010]$, and $[001]$, respectively. The laboratory coordinate system (X, Y, Z) is also defined in Fig. 1(B). Due to different symmetry of the surface, there are two mirror planes which are perpendicular to the surface (100) and lie along the $[011]$ and $[0\bar{1}1]$ axes. To understand the surface symmetry of the GaP(100), a surface coordinate system (ξ, η, ϵ) is defined in Fig. 1(B), where ξ, η and ϵ represent the $[011]$, $[0\bar{1}1]$, and $[100]$ axes, respectively. Thus, both the a axis in the bulk coordinate and the ϵ axis in the surface coordinates are perpendicular to the (100) surface, and lie along the Z axis in the laboratory coordinates. We define ϕ as an azimuthal rotational angle, corresponding to the angle of the $[011]$ symmetry axis away from the X axis as displayed in Fig. 1(C). ϕ is defined to be 0° when the $[011]$ direction is along the X axis, and 90° when the $[0\bar{1}1]$ is along the Y axis. The rotation of the azimuthal angle is counterclockwise. Since the angle between the b & c axes and the $[011]$ axis is 45° , the b and c principal axes are along the $\phi - 45^\circ$ and $\phi + 45^\circ$, respectively.

ESFG is a second-order non-linear optical process, in which two different photons of frequencies, $\omega_{\#}$ & $\omega_{\#}$, and their momenta, k_1 & k_2 , interact with matters to produce a new photon of a frequency $\omega_{\$}$ with momentum k_3 . Unlike VSFG, neither of the two frequencies is resonant with vibrations of chemical groups. The two beams propagate in the XZ plane in the laboratory coordinates system, constructing an incident plane where the Z axis is the surface normal (see Fig. 1(B)). In our case, a SWIR light ($\omega_{\#} = \omega_{\%&'(\cdot)}$) and a visible light ($\omega_{\#} = \omega_{\%*+}$) are incident on the GaP(100) surface, producing an ESFG signal light ($\omega_{\$} = \omega_{\%-\cdot}$) with both the energy and momentum conservations. $\alpha_{\#}$ and $\alpha_{\#}$ are incident angles with respect to the surface normal for the SWIR and visible beams. $\alpha_{\$}$ is the reflection angle for the ESFG beam with respect to the surface normal. γ_i ($i = 1, 2, 3$) is the refraction angle with respect to the surface normal for the ESFG, visible, and SWIR beams, respectively. S and P polarizations are defined to be perpendicular to or parallel to the incident plane, respectively.

The intensity of ESFG is intimately related to macroscopic effective surface susceptibility $\chi_{011}^{(\#)}$, which is given by^{115, 116}

$$I(\omega_{\$}) = \frac{45! \cdot 6! \cdot (+789!)}{:\#; \$ (6!); \$ (6\$); \$ (6'')} 9 \chi_{011}^{(\#)} 9^{\#} I(\omega_{\#}) I(\omega_{\#}) \quad (1)$$

where ω'' , $\omega_{\#}$, and $\omega_{\$}$ represent the frequencies of a SWIR pulse, a visible pulse, and an ESFG signal, respectively, and $n_{<}(\omega_i)$ is the refractive index of the medium (air (n''), bulk ($n_{\#}$) and surface ($n^{\pm}$),) at a frequency ω_i ($i = 1, 2, 3$).^{115, 116}

$$\chi_{011}^{(\#)} = [e(\omega_{\$}) \cdot \mathbf{L}(\omega_{\$})] \cdot \chi_{011,?@A}^{(\#)} : [e(\omega'') \cdot \mathbf{L}(\omega'')] \cdot [e(\omega_{\#}) \cdot \mathbf{L}(\omega_{\#})] \quad (2)$$

where $e(\omega_i)$ is the unit electric field vector for the light beam at frequency ω_i at the surface, $\mathbf{L}(\omega_i)$ is the Fresnel transmission tensor at frequency ω_i as formulated in Supporting Information, and $\chi_{011,?@A}^{(\#)}$ is the susceptibility in the laboratory coordinates system (X, Y, Z).

As a second-order process, ESFG is only sensitive to non-centrosymmetric structures. In bulk with a center of symmetry, ESFG is forbidden. Within the electric dipole approximation, ESFG is inherently surface specific and becomes a useful tool for surface analysis. However, in materials with non-centrosymmetric structures such as GaP, bulk contributions cannot be ignored due to the asymmetry in the bond between Ga and adjacent P atoms. In addition to dipole-allowed responses, quadrupole contributions from surface and bulk exist. For n -type and p -type doping GaP(100), surface charge induced ESFG responses are also included. As such, the effective susceptibility is the sum of both bulk and surface susceptibilities.¹¹⁷

$$\chi_{011}^{(\#)} = \chi_{BC}^{(\#)} + \chi_{BD}^{(\#)} + \chi_{\%C}^{(\#)} + \chi_{\%D}^{(\#)} + \chi_{\%E}^{(\#)} \quad (3)$$

where $\chi_{BC}^{(\#)}$, $\chi_{BD}^{(\#)}$, $\chi_{\%C}^{(\#)}$, $\chi_{\%D}^{(\#)}$, and $\chi_{\%E}^{(\#)}$ are macroscopic susceptibilities for bulk dipoles, bulk quadrupoles, surface dipoles, surface quadrupoles, and surface charges, respectively. The derivations for $\chi_{BD}^{(\#)}$ and $\chi_{\%D}^{(\#)}$ are found in Supporting Information. We shall discuss $\chi_{BC}^{(\#)}$, $\chi_{\%C}^{(\#)}$, and $\chi_{\%E}^{(\#)}$ as follows.

1. Bulk dipole susceptibilities, $\chi_{BC}^{(\#)}$.

The macroscopic susceptibility tensors of bulk dipoles, $\chi_{BC}^{(\#)}$, are related to the microscopic hyperpolarizabilities, $\beta_{FG}^{(\#)}$ of the crystal. There are six non-zero elements of the total of 27 second-order nonlinear bulk crystal hyperpolarizability tensors $\beta_{FG}^{(\#)}$ for $\bar{4}3m$ (T_H) symmetry, namely, $\beta_{IJ:}^{(\#)} = \beta_{I:I}^{(\#)} = \beta_{J:I}^{(\#)} = \beta_{J:I}^{(\#)} = \beta_{:IJ}^{(\#)} = \beta_{:II}^{(\#)} = \beta_{:II}^{(\#)}$,^{116, 118, 119} where a , b , and c refer to the principal axes of the crystal. In the

laboratory coordinates (X, Y, Z) , the macroscopic susceptibility tensors for bulk dipoles, $\chi_{BC}^{(\#)}$, are related to bulk hyperpolarizabilities, $\beta_{FG}^{(\#)}$, in the crystal coordinates (a, b, c) by¹²⁰

$$\chi_{BC,?@AKL,M,N}^{(\#)} = \sum R_{?/} R_{@F} R_{AG} \beta_{FGKI,J,:}^{(\#)} \quad (4)$$

where $R_{?/}$, $R_{@F}$, and R_{AG} denote a matrix element in the Euler transformation from the laboratory coordinates (X, Y, Z) to the crystal coordinates (a, b, c) as described in Supporting Information. For a cubic crystal of GaP, six susceptibilities are nonvanishing, including $\chi_{BC,LLN}^{(\#)}$, $\chi_{BC,LNL}^{(\#)}$, $\chi_{BC,NLL}^{(\#)}$, $\chi_{BC,MMN}^{(\#)}$, $\chi_{BC,MNM}^{(\#)}$, and $\chi_{BC,NMM}^{(\#)}$.^{116, 121} The bulk dipole susceptibilities take the form of¹⁰⁵

$$\begin{aligned} \chi_{BC,LLN}^{(\#)} &= \chi_{BC,LNL}^{(\#)} = \chi_{BC,NLL}^{(\#)} = \beta_{IJ:}^{(\#)} \times \cos 2\phi \\ \chi_{BC,MMN}^{(\#)} &= \chi_{BC,MNM}^{(\#)} = \chi_{BC,NMM}^{(\#)} = \beta_{IJ:}^{(\#)} \times (-\cos 2\phi). \end{aligned} \quad (5)$$

Experimentally, ESFG measurements of surfaces and interfaces are usually implemented in a reflection geometry at certain incident angles. As such, not all of the laboratory susceptibilities are directly measured by polarized experiments. A usual way is to introduce wavevector propagating coordinates (K, S, P) , where K denotes the direction of wavevectors of light beams. Four commonly used independent wave-propagating susceptibilities are typically employed in SFG experiments: $\chi_{BC,\% \% 0}^{(\#)}$, $\chi_{BC,\% 0 \%}^{(\#)}$, $\chi_{BC,0 \% \%}^{(\#)}$, and $\chi_{BC,000}^{(\#)}$. These are related to those from the laboratory susceptibilities by incident angles and Fresnel factors, and are expressed as^{117, 122}

$$\begin{aligned} \chi_{BC,\% \% 0}^{(\#)} &= L_{MM}(\omega_{\$}) L_{MM}(\omega_{\#}) L_{NN}(\omega_{\#}) \sin \alpha_{\#} \chi_{BC,MMN}^{(\#)} \frac{1}{-i\Delta k_P} \\ \chi_{BC,\% 0 \%}^{(\#)} &= L_{MM}(\omega_{\$}) L_{NN}(\omega_{\#}) L_{MM}(\omega_{\#}) \sin \alpha_{\#} \chi_{BC,MNM}^{(\#)} \frac{1}{-i\Delta k_P} \\ \chi_{BC,0 \% \%}^{(\#)} &= L_{NN}(\omega_{\$}) L_{MM}(\omega_{\#}) L_{MM}(\omega_{\#}) \sin \alpha_{\$} \chi_{BC,MMN}^{(\#)} \frac{1}{-i\Delta k_P} \\ \chi_{BC,000}^{(\#)} &= (-L_{LL}(\omega_{\$}) L_{LL}(\omega_{\#}) L_{NN}(\omega_{\#}) \cos \alpha_{\$} \cos \alpha_{\#} \sin \alpha_{\#} \chi_{BC,LLN}^{(\#)} \\ &\quad - L_{LL}(\omega_{\$}) L_{NN}(\omega_{\#}) L_{LL}(\omega_{\#}) \cos \alpha_{\$} \sin \alpha_{\#} \cos \alpha_{\#} \chi_{BC,LNL}^{(\#)} \\ &\quad + L_{NN}(\omega_{\$}) L_{LL}(\omega_{\#}) L_{LL}(\omega_{\#}) \sin \alpha_{\$} \cos \alpha_{\#} \cos \alpha_{\#} \chi_{BC,NLL}^{(\#)}) \frac{1}{Q/\Delta G_{\%}}. \end{aligned} \quad (6)$$

2. Surface dipole susceptibilities, $\chi_{\%C}^{(\#)}$.

The hyperpolarizabilities in the surface coordinates (ξ, η, ε) are projected into the macroscopic susceptibility tensors $\chi_{\%C}^{(\#)}$ in the laboratory coordinates (X, Y, Z) , via^{116, 121}

$$\chi_{\%C,?@AKL,M,N}^{(\#)} = \sum R_{?S} R_{@T} R_{A;K\xi,\eta,\varepsilon} \beta_{ST;K\xi,\eta,\varepsilon}^{(\#)} \quad (7)$$

where $R_{\gamma/}$, R_{OF} , and R_{AG} denote a matrix element in the Euler transformation from the laboratory coordinates (X, Y, Z) to the surface coordinates (ξ, η, ε) as described in Supporting Information.

The surface symmetry of GaP(100) could be either C_{2v} or C_{4v} . Under a C_{2v} symmetry for the topmost and sublayers, there are seven independent non-zero terms, $\beta_{\text{UU}}^{(\#)}, \beta_{\text{VV}}^{(\#)}, \beta_{\text{WW}}^{(\#)}, \beta_{\text{UV}}^{(\#)}, \beta_{\text{VW}}^{(\#)}, \beta_{\text{WU}}^{(\#)}$ and $\beta_{\text{VU}}^{(\#)}$.¹¹⁶ The microscopic hyperpolarizability tensors, $\beta^{(\#)}$, for C_{2v} possesses 7 independent elements: $\beta_{\text{UUU}}^{(\#)}, \beta_{\text{UUU}}^{(\#)}, \beta_{\text{VVU}}^{(\#)}, \beta_{\text{WWW}}^{(\#)}, \beta_{\text{WWW}}^{(\#)}, \beta_{\text{WWW}}^{(\#)}$ and $\beta_{\text{VVV}}^{(\#)}$. In the case of GaP(100) surfaces with a C_{2v} symmetry, the macroscopic susceptibility tensors $\chi_{\%C}^{(\#)}$ terms are given by¹⁰⁵

$$\begin{aligned}\chi_{\%C, \text{LLN}}^{(\#)}(\omega_{\text{I}}) &= \frac{1}{2} [0\beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}}) - \beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}})P \cos 2\phi + (\beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}}) + \beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}}))] \\ \chi_{\%C, \text{LNL}}^{(\#)}(\omega_{\text{I}}) &= \frac{1}{2} [0\beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}}) - \beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}})P \cos 2\phi + (\beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}}) + \beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}}))] \\ \chi_{\%C, \text{NLL}}^{(\#)}(\omega_{\text{I}}) &= \frac{1}{2} [0\beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}}) - \beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}})P \cos 2\phi + (\beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}}) + \beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}}))] \\ \chi_{\%C, \text{MMN}}^{(\#)}(\omega_{\text{I}}) &= \frac{1}{2} [0\beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}}) - \beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}})P \cos 2\phi + (\beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}}) + \beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}}))] \\ \chi_{\%C, \text{MNM}}^{(\#)}(\omega_{\text{I}}) &= \frac{1}{2} [0\beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}}) - \beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}})P \cos 2\phi + (\beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}}) + \beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}}))] \\ \chi_{\%C, \text{NNM}}^{(\#)}(\omega_{\text{I}}) &= \frac{1}{2} [0\beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}}) - \beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}})P \cos 2\phi + (\beta_{\text{WWW}}^{(\#)}(\omega_{\text{I}}) + \beta_{\text{UUU}}^{(\#)}(\omega_{\text{I}}))] \\ \chi_{\%C, \text{NNN}}^{(\#)}(\omega_{\text{I}}) &= \beta_{\text{VVV}}^{(\#)}(\omega_{\text{I}}).\end{aligned}\tag{8}$$

As in Eq. 6, four independent wave-propagating susceptibilities are typically employed in SFG experiments: $\chi_{\%C, \%O}^{(\#)}, \chi_{\%C, \%O}^{(\#)}, \chi_{\%C, \%O}^{(\#)}$, and $\chi_{\%C, 000}^{(\#)}$. These are related to the laboratory susceptibilities by incident angles and Fresnel factors, and are expressed as⁵⁷

$$\begin{aligned}\chi_{\%C, \%O}^{(\#)} &= L_{\text{MM}}(\omega_{\text{I}})L_{\text{MM}}(\omega_{\text{V}})L_{\text{NN}}(\omega_{\text{S}}) \sin \alpha_{\text{I}} \chi_{\%C, \text{MMN}}^{(\#)} \\ \chi_{\%C, \%O}^{(\#)} &= L_{\text{MM}}(\omega_{\text{I}})L_{\text{NN}}(\omega_{\text{V}})L_{\text{MM}}(\omega_{\text{S}}) \sin \alpha_{\text{V}} \chi_{\%C, \text{MNM}}^{(\#)} \\ \chi_{\%C, \%O}^{(\#)} &= L_{\text{NN}}(\omega_{\text{I}})L_{\text{MM}}(\omega_{\text{V}})L_{\text{MM}}(\omega_{\text{S}}) \sin \alpha_{\text{S}} \chi_{\%C, \text{MMN}}^{(\#)} \\ \chi_{\%C, 000}^{(\#)} &= -L_{\text{LL}}(\omega_{\text{I}})L_{\text{LL}}(\omega_{\text{V}})L_{\text{NN}}(\omega_{\text{S}}) \cos \alpha_{\text{I}} \cos \alpha_{\text{V}} \sin \alpha_{\text{S}} \chi_{\%C, \text{LLN}}^{(\#)} \\ &\quad -L_{\text{LL}}(\omega_{\text{I}})L_{\text{NN}}(\omega_{\text{V}})L_{\text{LL}}(\omega_{\text{S}}) \cos \alpha_{\text{I}} \sin \alpha_{\text{V}} \cos \alpha_{\text{S}} \chi_{\%C, \text{LNL}}^{(\#)} \\ &\quad +L_{\text{NN}}(\omega_{\text{I}})L_{\text{LL}}(\omega_{\text{V}})L_{\text{LL}}(\omega_{\text{S}}) \sin \alpha_{\text{I}} \cos \alpha_{\text{V}} \cos \alpha_{\text{S}} \chi_{\%C, \text{NLL}}^{(\#)} \\ &\quad +L_{\text{NN}}(\omega_{\text{I}})L_{\text{NN}}(\omega_{\text{V}})L_{\text{NN}}(\omega_{\text{S}}) \sin \alpha_{\text{I}} \sin \alpha_{\text{V}} \sin \alpha_{\text{S}} \chi_{\%C, \text{NNN}}^{(\#)}.\end{aligned}\tag{9}$$

On the other hand, only the four terms are nonvanishing for C_{4v} symmetry at the top-most layer, namely, $\beta_{UVV}^{(\#)} = \beta_{VWV}^{(\#)}$, $\beta_{UVU}^{(\#)} = \beta_{VWU}^{(\#)}$, $\beta_{VUU}^{(\#)} = \beta_{VWW}^{(\#)}$, and $\beta_{VW}^{(\#)}$. The derivation for the C_{4v} symmetry can be found in Supporting Information.

3. Surface charge induced susceptibilities, $\chi_{\%E}^{(\#)}$.

Surface charges can contribute to ESFG responses for doped semiconductors. The surface charge induced susceptibility, $\chi_{\%E}^{(\#)}$, is the product of third-order susceptibility, $\chi^{(\$)}$, and electric fields, E , within the coherence length of the ESFG process, $1/\Delta k_p$, specifically, $\chi^{(\$)}E$. When the electric field exists only along the surface normal (E_z), four nonvanishing elements of $\chi^{(\$)}$ are as follows: $\chi_{NNNN}^{(\$)}$; $\chi_{LLNN}^{(\$)} = \chi_{MMNN}^{(\$)}$; $\chi_{LNLN}^{(\$)} = \chi_{MNMN}^{(\$)}$; and $\chi_{NLLN}^{(\$)} = \chi_{NMMN}^{(\$)}$. The azimuth-dependent $\chi^{(\$)}$ elements follow those from surface dipole induced ESFG responses as shown in Eq. 8:⁹⁴

$$\begin{aligned}\chi_{\%E,NNN}^{(\#)} &= \chi_{NNNN}^{(\$)} E_N \\ \chi_{\%E,LLN}^{(\#)} &= \chi_{\%E,MMN}^{(\#)} = \chi_{MMNN}^{(\$)} E_N = \chi_{LLNN}^{(\$)} E_N \\ \chi_{\%E,LNL}^{(\#)} &= \chi_{\%E,MNM}^{(\#)} = \chi_{LNLN}^{(\$)} E_N = \chi_{MNMN}^{(\$)} E_N \\ \chi_{\%E,NLL}^{(\#)} &= \chi_{\%E,NMM}^{(\#)} = \chi_{NLLN}^{(\$)} E_N = \chi_{NMMN}^{(\$)} E_N.\end{aligned}\tag{10}$$

We assume that Z -dependent electric potential is written as $\Phi(z) = \Phi(0)e^{Qz}$, where $\Phi(0)$ is the surface potential with respect to the flat band, and κ is the band bending depth caused by either depletion or accumulation in the surface region of GaP in the presence of doping. As a result, the surface charge-induced ESFG responses are expressed as^{99, 123-126}

$$\chi_{\%E}^{(\#)} = \frac{X}{XQ/\Delta G_{\%}} \chi^{(\$)} \Phi(0) \Delta k_p.\tag{11}$$

It is noted that Eq. 11 is slightly different from those reported in the literature,^{123, 124, 126} in that it is necessary to include additional Δk_p for the purpose of the correct unit. We further decompose Eq. 11 into the real, $\chi_{\%E,Y}^{(\#)}$, and imaginary parts, $\chi_{\%E,Z}^{(\#)}$, as follows:^{99, 123, 124}

$$\begin{aligned}\chi_{\%E,Y}^{(\#)} &= \frac{X''}{X''Z\Delta G_{\%}} \chi^{(\$)} \Phi(0) \Delta k_p \\ \chi_{\%E,Z}^{(\#)} &= \frac{X\Delta G_{\%}}{X''Z\Delta G_{\%}} \chi^{(\$)} \Phi(0) \Delta k_p.\end{aligned}\tag{12}$$

As seen in Eq. 12, only the imaginary part dominates when $\kappa \ll \Delta k_p$, and only the real part dominates when $\kappa \gg \Delta k_p$, and both the real and imaginary parts exist when $\kappa \sim \Delta k_p$.

4. ESFG intensity.

The azimuth-dependent ESFG intensities for GaP(100) are given by,

$$I_{[\lambda]}(\phi) \propto 9\chi_{011}^{(\#)}(\phi)g^{\#} = 9\chi_{-SG,I;/a}^{(\#)}(\phi) + \chi_{-SG,/ab}^{(\#)} + \chi_{\backslash'c1I:0,I;/a}^{(\#)}(\phi) + \chi_{\backslash'c1I:0,/ab}^{(\#)}g^{\#} \quad (13)$$

where subscripts “*anis*” and “*iso*” represent anisotropic and isotropic components of both bulk and surface susceptibilities, respectively. In our case, the $\chi_{BD}^{(\#)}$ and $\chi_{\%D}^{(\#)}$ are assumed to be negligible since the contributions from bulk quadrupoles and surface quadrupoles do not change with doping. No isotropic component occurs in Eq. 13. Thus, we consider contributions of effective susceptibilities only from bulk dipoles (anisotropic, $\chi_{011,BC,I;/a}^{(\#)}(\phi)$), surface dipoles (isotropic, $\chi_{011,\%C,/ab}^{(\#)}$ and anisotropic, $\chi_{011,\%E,I;/a}^{(\#)}(\phi)$), and surface charges (isotropic, $\chi_{011,\%E,/ab}^{(\#)}$, and anisotropic, $\chi_{011,\%E,I;/a}^{(\#)}(\phi)$) only. Thus, azimuth-dependent ESFG intensities take the form of

$$I_{[\lambda]}(\phi) \propto \frac{\chi_{\&',',,)*,+,,-}^{(e)}}{Q/\Delta G_{\%}} + \chi_{011,\%E,I;/a}^{(\#)}(\phi) + \chi_{011,\%C,I;/a}^{(\#)}(\phi) + \chi_{011,\%E,/ab}^{(\#)} + \chi_{011,\%C,/ab}^{(\#)}g^{\#} \quad (14)$$

All the anisotropic parts follow a 2-fold symmetry in the surface plane, even though the latter two are not complex under non-resonant conditions. For non-negligible isotropic parts, the azimuth-dependent ESFG responses are expected to follow a 4-fold symmetry. Since both the susceptibilities for the surface charges and surface dipoles have the same isotropic and anisotropic features, we could combine them into $\chi_{011,\%EC,I;/}^{(\#)}(\phi)$ and $\chi_{011,\%EC,/ab}^{(\#)}$, and further simplify Eq.14 into,

$$I_{[\lambda]}(\phi) \propto \frac{\chi_{\&',',,)*,+,,-}^{(e)}}{Q/\Delta G_{\%}} + \chi_{011,\%EC,I;/}^{(\#)}(\phi) + \chi_{011,\%EC,/ab}^{(\#)}g^{\#} \quad (15)$$

It is noted that all $\chi_{BC,I;/a}^{(\#)}(\phi)$, $\chi_{\%EC,I;/a}^{(\#)}(\phi)$, and $\chi_{\%EC,/ab}^{(\#)}$ could be complex when resonant with electronic transitions. For each azimuthal angle, intensities of an ESFG spectrum are written as

$$I(\omega, \phi) \propto 9\chi_{f,/ab}^{(\#)} + \chi_{f(I;/a)}^{(\#)}(\phi) + \sum_j \frac{g_{1,+,-}^{(e)}}{6Q6} \frac{(e)}{Q/h} + \sum_j \frac{g_{1,-,2}}{6Q6} \frac{(e)}{Q/h}g^{\#} \quad (16)$$

For a given ϕ , we further obtained as follows:

$$I(\omega) \propto 9C + \sum_j \frac{g_1}{6Q6} \frac{(e)}{Q/h}g^{\#} \quad (17)$$

where $\chi_{f(i)/ab}^{(\#)}$ and $\chi_{f(i);/a}^{(\#)}$ are the non-resonant complex susceptibilities for isotropic and anisotropic components, A_R represents resonant amplitude of hyperpolarizability, ω_i denotes the i th electronic transition frequency, and Γ denotes the damping rate of electronic transitions. Both surface and bulk contribute to either resonant or non-resonant components of the total macroscopic susceptibility, depending on if electronic transitions are of surface or bulk origin. There are four possible pathways in the process of ESFG, including off-resonant/off-resonant, off-resonant/resonant, resonant/off-resonant, and resonant/resonant.¹²⁷ In the case of GaP under our experimental conditions, off-resonant/resonant accounts for the resonant ESFG in Eq. 16, as schematically shown in Figure 1(D).

Experimental Section

Laser system. A detailed description of steady-state ESFG experiments has been reported previously.^{70, 71, 128} Briefly, a fundamental light centered at 797 nm from a 1 kHz Ti:Sapphire amplifier system (UpTek Solutions) was used. The output energy of the laser was 4 mJ per pulse with a pulse duration of 100 fs. A major portion of 2.0 mJ was passed through an etalon to generate a picosecond pulse of 8 cm⁻¹. A small portion of 1.5 mJ was used to generate a shortwave IR (SWIR) pulse from a home-built broadband optical parametric amplifier (BOPA).^{70, 71, 128} The remaining fundamental pulse of 0.5 mJ was doubly converted with a Beat Barium borate (BBO) crystal into 400 nm as a pump pulse. The time delay between the picosecond pulse and the SWIR was controlled by a motorized translation stage (Klinger).

Optical layout. The picosecond pulse of 40 μ J and the SWIR of 10 μ J were incident on a sample at 60° and 45°, respectively, with respect to the surface normal. The spot sizes were set to be 510 μ m for the picosecond and 300 μ m for the SWIR, separately. Three polarizers were used to select different polarization combinations for the ESFG, picosecond pulse, and the SWIR. The polarization combinations of SSP, SPS, PSS, and PPP were defined in an order of increasing wavelength for the three beams. In the SWIR light path, an additional 1000 nm long-pass filter was placed before the samples to remove some visible lights generated by the optical elements in the BOPA.

Collection of ESFG spectra. A spectrometer (Kymera 328i-C, Andor Technology) with a thermally cooled charge-coupled device (CCD) (IDus DU420A-BVF, 1024 $\times$ 255, Andor Technology) was used to collect both ESFG and ESHG spectra. Typically, an exposure time of 60 s and 5 s were used for spectra at azimuthal angles of 45° and 0°, respectively.

Azimuth-dependent ESFG measurements. A motorized rotational stage (Newport) was used to control azimuthal angles of the GaP samples. To guarantee no wobbling in the rotation, the samples were positioned in the center of the stage. A custom Labview program was made to communicate with the rotation stage via a computer in azimuth-dependent ESFG experiments. Steady-state ESFG spectra were normalized by silver thin films (Thorlabs).

Phase measurements. Heterodyne detection (HD) of broadband SHG was used for phase measurements with the SWIR from 1150 nm to 1500 nm, using a short-pass (Edmund Optics) filter with a cutoff wavelength of 1500 nm.¹²⁹ The 2.9 μJ SWIR pulse was focused to be 130 μm in diameter using a lens with 25 cm focal length, followed by a 1000 nm long-pass filter. A z-cut α -quartz crystal (MTI) of 100 μm acted as a local oscillator (LO). The generated SHG signal from the LO and the transmitted fundamental beam maintained spatial collinearity when overlapped at surfaces. Glass slides as time delay generators were placed after the LO. A short pass filter of 900 nm (Thorlabs) was placed directly after the samples to remove the fundamental light for phase measurements. The polarization of the fundamental light was set to be S-polarized (S-in) or P-polarized (P-in), while that of the SHG light P-polarized (P-out). Thus, two polarization combinations of S-in/P-out and P-in/P-out were used in phase experiments. Typically, an exposure time of 5s was used for phase measurements. A routine Fourier analysis treatment yielded phase information for different azimuthal angles.^{93, 130, 131}

Samples. Both *n*-type GaP(100) S-doped $2\text{--}12 \times 10^{17} \text{ cm}^{-3}$ and *p*-type GaP(100) Zn-doped $4.0\text{--}5.2 \times 10^{17} \text{ cm}^{-3}$ were purchased from MTI. Silver thin films (PO1, Thorlabs) were used as received. Left-handed z-cut α -quartz crystals (Brightcrystals Technology INC.) were used in phase measurements.

Results

Azimuth-dependent ESFG from GaP(100). To investigate surface symmetry of GaP(100), azimuth-dependent ESFG experiments were carried out. The [011], [010], and [01 $\bar{1}$] axes for GaP(100) are defined to be 0°, 45°, and 90°, in a counterclockwise manner, as they are for GaAs.¹⁰⁵ Figure 2 shows pseudo-color 2D plots of PSS-polarized ESFG spectra of GaP(100) for *n*-type (A) and *p*-type (C) as a function of azimuthal angle. SPS and SSP polarization combinations are found in Figures S1. It is shown that all the ESFG responses exhibit 2-fold symmetry patterns at different wavelengths from 470 nm to 530 nm for both *n*-type and *p*-type GaP(100) crystals. Figures 2(B) and (D) show polar plots of PSS-polarization ESFG intensities as a function of azimuthal angle for both *n*-type and *p*-type GaP(100) at 490 nm. Eq. 5 shows that bulk dipole contributions exhibit 4-fold ESFG intensity as a function of azimuthal angle for GaP(100) if only bulk dipoles exist. Our experiments showed 2-fold azimuth-dependent patterns for all polarizations,

indicating that the surfaces components also contribute to the ESFG responses and exhibit a C_{2v} symmetry rather than a C_{4v} symmetry for both n -type and p -type GaP(100). The ESFG signals were not only from the topmost layer, but also from sublayers. These results are consistent with those for GaAs,^{95, 96, 105} suggesting that GaP(100) crystals have the same surface structures as GaAs.

As expected, the ESFG signals at 0° ($[011]$), 90° ($[01\bar{1}]$), 180° ($[0\bar{1}\bar{1}]$), and 270° ($[01\bar{1}]$) were dominated by bulk (bulk-dominant), while those at 45° ($[010]$), 135° ($[00\bar{1}]$), 225° ($[0\bar{1}0]$), and 315° ($[001]$) were dominated by isotropic surface components (surface-dominant). The surface-dominant ESFG signals were relatively weak. It is important to note that the maximum ESFG signals occur at 90° ($[01\bar{1}]$) and 270° ($[0\bar{1}\bar{1}]$) for n -type GaP(100), and at 0° ($[011]$) and 180° ($[0\bar{1}\bar{1}]$) for p -type GaP(100). The differences in the maximum ESFG signals suggest that the isotropic surface components carry positive or negative signs of the $\chi_{ab}^{(\#)}$ for the n - and p -type GaP(100) crystals. As formulated in Eq. 14, the isotropic surface components are from either surface charges and/or surface dipoles. However, from the intensity measurements, we could not differentiate them.

Phase Measurements of Surface and Bulk Contributions. To further identify signatures and the origins of the isotropic surface components, heterodyne detection of interfacial broadband electronic spectroscopy (HD-iES) was implemented.¹²⁹ We chose a wavelength range of 1140-1500 nm for our HD-iES experiments. As such, the broadband HD method can provide spectra ranging from 570 nm to 750 nm. In this wavelength range, the $\chi^{(\#)}$ of the GaP crystals only shows non-resonance contributions. Otherwise, the phases would jump once resonant with surface transitions, leading to the added complexity of separation of surface charge induced susceptibility, $\chi_{\%E}^{(\#)}$, and the surface dipole susceptibility, $\chi_{\%C}^{(\#)}$.

In our HD experiments, we used the left-handed z -cut α -quartz as a reference to measure the absolute phases of GaP since the absolute phase of $\chi_{i'Icjp,-}^{(\#)}$ for z -cut α -quartz is known to be -90° for S-in/P-out, as shown in Figure S2. Figure 3 shows the absolute phases as a function of azimuthal angle at 700 nm for the n -type (A) and p -type (C) GaP(100) crystals under S-in/P-out polarization combination. It is seen that the azimuth-dependent phases produce shifted phase cycles for the n -type GaP(100) between 270° and 90° , relative to those for the p -type GaP(100) between -90° and 90° . In fact, the phases of 270° and -90° are the same mathematically. It is surprising that the phases alternate differently for the n -type and p -type GaP(100) crystals.

To discover the origins for the shifted phase cycles along the surface-dominant axes for the n -type and p -type GaP(100) crystals, we carried out simulations by using Eq. 15. Experimentally, we could not differentiate $\chi_{\%E}^{(\#)}$ from $\chi_{\%C}^{(\#)}$, but only $\chi_{\%EC,I;/a}^{(\#)}$ from $\chi_{\%Ek,/ab}^{(\#)}$. The sign of $\chi_{BC}^{(\#)}$ along the bulk-dominant direction is negative from our previous phase measurements,¹²⁹ as confirmed in Figure S2. The signs of

$\chi_{BC}^{(\#)}$, $\chi_{\%C,I;/a}^{(\#)}$, and $\chi_{\%C,/ab}^{(\#)}$ remain unchanged with doping. On the other hand, $\chi_{\%E,/ab}^{(\#)}$ and $\chi_{\%E,I;/a}^{(\#)}$ could possibly change signs due to opposite electrical fields, as presented in Eq. 10. Thus, we kept the values of $\chi_{BC}^{(\#)}$ and $\chi_{\%EC,I;/}^{(\#)}$ to be -0.9 and 0.4, separately, while changing the values and signs of $\chi_{\%EC,/ab}^{(\#)}$ with both real and imaginary parts in the simulations. It was found that the imaginary part does not affect the trend of phase cycles with azimuthal angle. Furthermore, the azimuth-dependent phases exhibit significant phase jumps when only the real part of $\chi_{\%EC,/ab}^{(\#)}$ varies, and the anisotropic part, $\chi_{\%EC,I;/a}^{(\#)}$ slightly move the phases up or down along the bulk-dominant axes. Figure S3 shows the simulated azimuth-dependent phases for $\chi_{\%EC,/ab}^{(\#)}$ of 1, 0.1, 0.01, -0.01, 0.1, and -1, which includes both $\chi_{\%E,/ab}^{(\#)}$ and $\chi_{\%C,/ab}^{(\#)}$. These simulation results have two implications: 1) The contribution from the $\chi_{\%E,/ab}^{(\#)}$ was greater than that from the $\chi_{\%C,/ab}^{(\#)}$; 2) the surface charges changed signs from the *n*-type to the *p*-type GaP(100) crystals.

Figures 3 (B and D) shows the interference electronic spectra under the S-in/P-out polarization combination for *n*-type and *p*-type GaP(100) along the surface-dominant [010] directions, compared to those from a left-handed z-cut quartz. The interference peaks of both the *n*-type and *p*-type GaP under the S-in/P-out configuration show significant shifts relative to that for the left-handed quartz, one with phase lead, the other with phase lag. The phases along the surface-dominant directions differ by almost 180° between the *n*-type and *p*-type GaP(100). These experimental and simulation results indicate that surface charges have negative and positive signs for the *n*-type and *p*-type GaP(100), separately.

ESFG spectra measurements. To investigate spectral features from the bulk and surface, we normalized the static-state ESFG spectra for both *n*-type and *p*-type GaP(100). Figure 4 shows the normalized PSS-polarized ESFG spectra along the [010] axis (surface-dominant) for *n*-type (A) and *p*-type (C) under different polarization combinations, compared to those along the [011] axis (bulk-dominant) for *n*-type (B) and *p*-type (D). The ESFG spectra for SPS and SSP polarization combinations are found in Figure S4. It is seen that all the ESFG spectra appear to be similar under all the polarization combinations along the surface-dominant and bulk-dominant directions for both the *n*-type and *p*-type GaP crystals. A significant difference for those two directions is that the signals near the plateau which occurs at longer wavelength along the bulk-dominant directions were larger than those along the surface-dominant directions. These results indicate that the non-resonant parts along the bulk-dominant direction were bigger than those along the surface-dominant direction.

To reveal spectral peaks, all the ESFG spectra were fitted with Eq. 16. The fitting results are shown in Tables S1 and S2. It was found that ESFG spectra along both the bulk-dominant and surface-dominant directions exhibit three peaks with slight shifts for both *n*-type and *p*-type GaP(100), and the transition

strengths of the peaks for *n*-type GaP are slightly different from those for *p*-type GaP. The three peaks for the *n*-type GaP(100) are located at around 471 nm, 478 nm and 495 nm along the bulk-dominant direction, and near 470 nm, 480 nm and 500 nm along the surface-dominant direction. On the other hand, the three peaks for the *p*-type GaP(100) are located at around 473 nm, 486 nm, and 498 nm along the bulk-dominant direction, and with three peaks near 474 nm, 480 nm, and 500 nm along the surface-dominant direction. These ESFG spectra exhibit three similar peaks along both the bulk-dominant and surface-dominant directions, suggesting that the peaks might have similar origins.

There exist two possibilities in the assignment of the three peaks for both the bulk-dominant and surface-dominant ESFG spectra of the GaP(100) crystals. One possibility is that all the peaks are of bulk origins, or they all come from the crystal surface. The latter of the surface-originated peaks is preferred based on the arguments that follow. First, the ESFG spectra along the bulk-dominant direction were found to be dominated by non-resonant parts, which were due to bulk dipole $\chi_{\text{BG}}^{(\#)}$. Spectral contributions from the resonant parts were much smaller than those from non-resonant ones, as shown in Tables S1 and S2. Second, our transient ESFG experiments showed that the carriers in the GaP bulk were not as photoexcited as expected. Figure S5 compares transient spectra at a time delay of 100 ps along the bulk-dominant and surface-dominant directions for the *n*- and *p*-type GaP(100) through transient ESFG. It was found that the percentages of ground state bleaching (GSB) of these peaks along the bulk-dominant directions were much less than those along the surface-dominant directions. If the peaks were due to transitions from the bulk, the percentage of GSB is expected to be much larger. These kinetics results suggest that only surface carriers were populated. Lastly, the GaP crystals are an indirect transition semiconductor, and no direct transitions are allowed in bulk in the examined wavelength region. Together, these three peaks were suggested to originate primarily from transitions of surface states for the GaP(100) crystals.

Discussion

In the case of free GaP surfaces, surface states in the band gap originate from reconstruction-induced bonds and surface charge-induced states. These electronic states are localized with discrete energy levels, either empty, partially occupied, or fully occupied. In doped GaP surfaces, charges primarily induce surface states. Our experimental findings show that surface states carry negative charges for the *n*-type and positive charges for the *p*-type GaP, separately, as schematically displayed in Figure 5. For the *n*-type GaP, the acceptor-type surface states were located at $E_{\text{as}1} = 2.64$ eV (peak at 470 nm), $E_{\text{as}2} = 2.58$ eV (peak at 480 nm) and $E_{\text{as}3} = 2.48$ eV (peak at 500 nm), above the valence-band edge. For the *p*-type GaP, the donor-type surface states were located at $E_{\text{ds}1} = 0.16$ eV (peak at 474 nm), $E_{\text{ds}2} = 0.20$ eV (peak at 480 nm) and $E_{\text{ds}3} = 0.30$ eV (peak at 500 nm), above the valence-band edge. Since the GaP is an indirect semiconductor, these

surface states are not necessarily located at the Γ point. From our results, the three ESFG peaks were assigned to be transitions from the VB to the three acceptor-type surface states for the *n*-type GaP, and from the donor-type surface states to the CB for the *p*-type GaP.¹³²

Now that we have known the phases along the surface-dominant directions, we quantitatively analyzed the $\chi_{BG}^{(\#)}$, $\chi_{\%EC,I;/a}^{(\#)}$, and $\chi_{\%EC,/ab}^{(\#)}$ by fittings of Eq. 15 into the three surface transitions for *n*-type and *p*-type GaP(100) crystals, as shown in Figure S6. We were able to obtain the relative values of $\chi_{BC}^{(\#)}$, $\chi_{\%EC,/ab}^{(\#)}$ and $\chi_{\%EC,I;/a}^{(\#)}$ for each transition as shown in Table S3. These values slightly varied for the three peaks, likely due to complex contributions of surface charge induced responses, as shown in Eq. 12. It was found that the bulk contributions were comparable to those of the anisotropic surface components. Furthermore, the isotropic surface components were found to be much smaller than the anisotropic surface components. The isotropic surface components are dominated by surface charge induced responses.

For semiconductor surfaces, bulk contributions always complicate interpretation of surface SFG and SHG, impeding wide applications of the techniques. Generally, only SFG or SHG intensity measurements could hardly differentiate surface from bulk. The combination of spectral information with phase experiments has enabled us to quantify contributions from surface, bulk, or both with azimuthal angle for *n*-type and *p*-type GaP(100). Our results indicate that the electronic transitions are dominated by surfaces for any azimuthal angles in GaP(100), instead of bulk dipoles.

Conclusions

We have combined azimuth-dependent ESFG spectroscopy with phase measurements to investigate surface states for both *n*-type and *p*-type GaP(100) photoelectrodes. Azimuth-dependent ESFG intensities showed that the GaP(100) surfaces exhibit C_{2v} symmetry. These ESFG spectroscopic studies have also enabled us to identify three surface states for both the *n*-type and *p*-type the GaP crystals., and our phase measurements revealed the nature of the surface states. The surface states were found to originate from surface charge induced local states which carry different charges: negative for the *n*-type and positive for the *p*-type GaP. We have also completed a thorough analysis of surface ESFG theory by considering bulk dipoles and quadrupoles, surface dipoles and quadrupoles, and surface charges. Our experiments support that only bulk dipoles, surface dipoles, and surface charges contribute to the ESFG responses. We have further quantified surface and bulk contributions, based on the spectral and phase measurements, showing that the surface transitions dominate at all the azimuthal angles. These unique surface approaches will potentially help us understand surface behaviors of other semiconductors in the processes of photocatalysis and photoelectrocatalysis.

Supporting Information

The supporting information contains the Fresnel transmission tensor and Euler transformation, the derivation of bulk and surface quadrupole contributions ($\chi_{BD}^{(\#)}$ and $\chi_{\%D}^{(\#)}$) and the derivation of the susceptibilities for C_{4v} symmetry. The following supporting figures and tables are provided in the supporting information: Pseudo-color 2D plot of intensities from *n*-type and *p*-type GaP(100) (SPS and SSP) as a function of azimuthal angle, Figure S1; Interference *b*-ESHG spectra for *n*-type and *p*-type GaP(100) (S-in/P-out) along the bulk-dominant axes, Figure S2; The simulation of the phases as a function of azimuthal angle, Figure S3. SSP and SPS ESFG spectra for *n*-type and *p*-type GaP(100) along the [011] axis (bulk-dominant) and [010] axis (surface-dominant), Figure S4. Bleaching comparison of bulk and surface, Figure S5. Fitting of the intensities from *n*-type and *p*-type GaP(100) as a function of azimuthal angle at three resonance peaks, Figure S6. Fitting results of *n*-type and *p*-type GaP(100) static spectra, Table S1 and Table S2. Fitting results of the intensities from *n*-type and *p*-type GaP(100) as a function of azimuthal angle at three resonance peaks, Table S3.

Acknowledgments

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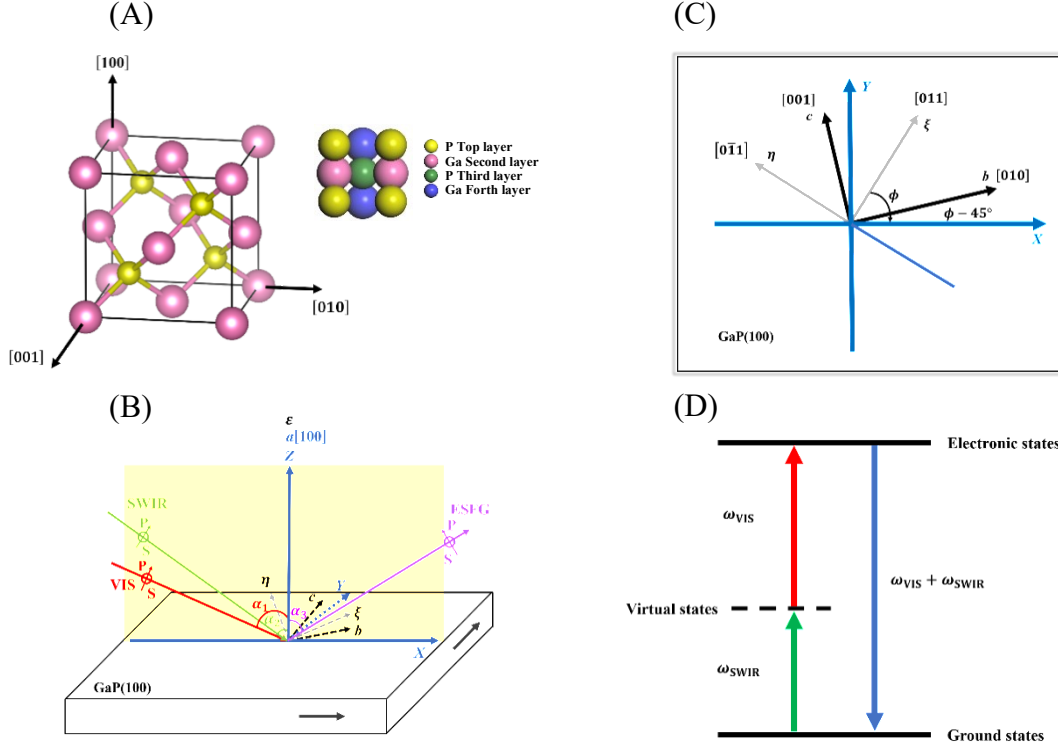


Figure 1. (A) Schematic of a unit cell of GaP. The top view of the GaP(100) surface is shown in the inset. (B) Schematic of the ESFG experimental setup, where a visible beam, a SWIR beam, and a resultant ESFG beam are configured. Three coordinate systems including the laboratory coordinates (X, Y, Z), crystal coordinates (a, b, c), and surface coordinates (ξ, η, ε) in GaP(100) are defined. (C) Azimuthal angle, ϕ , is defined to be the angle of the $[011]$ symmetry axis away from the X axis. ϕ is defined to be 0° when the $[011]$ direction is along the X axis and ϕ is 90° when the $[01\bar{1}]$ is along the Y axis. The rotation of the azimuthal angle is counterclockwise. The b and c principal axes are along $\phi - 45^\circ$ and $\phi + 45^\circ$, respectively. (D) Energy diagram of ESFG in the case of off-resonance/resonance for GaP(100) under our experimental conditions.

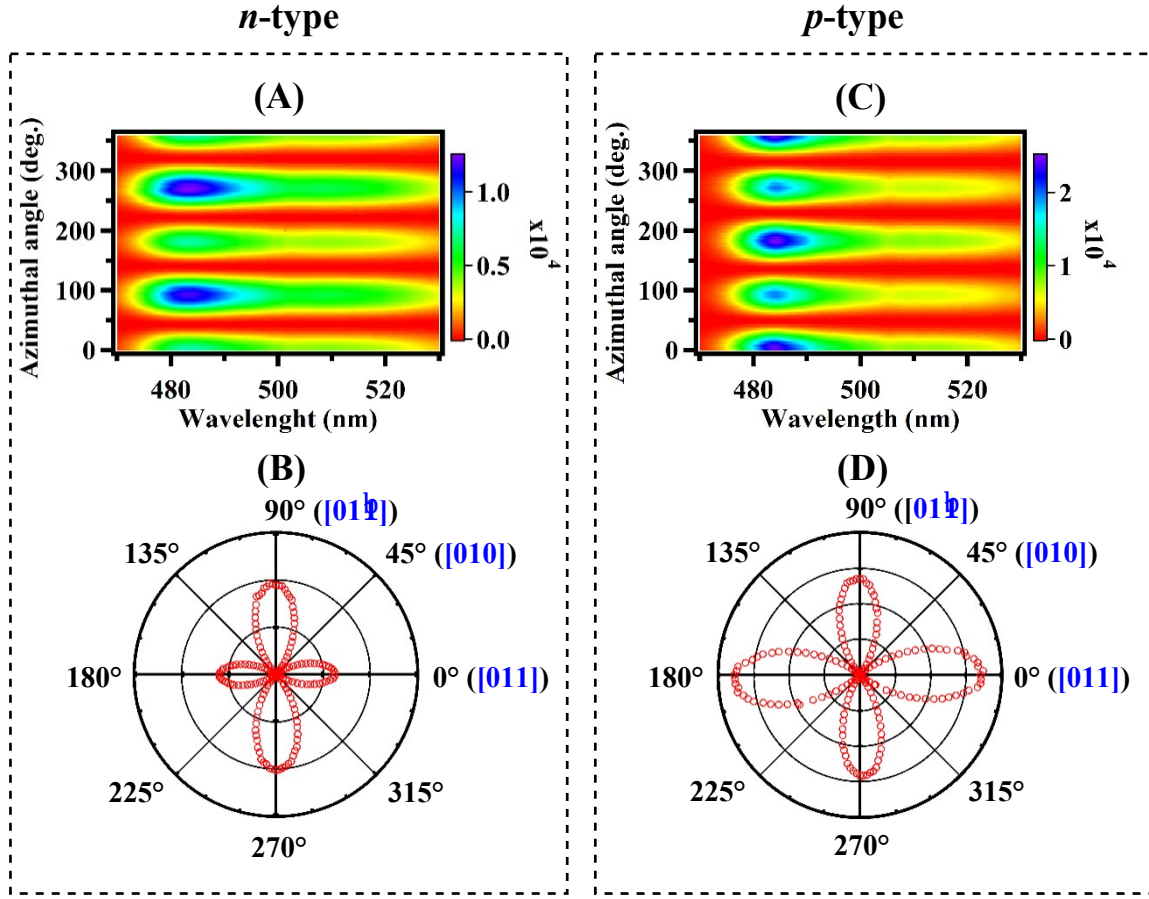


Figure 2. Pseudo-color 2D plot of PSS-polarized ESFG intensities (unnormalized) for *n*-type (A) and *p*-type GaP(100) (C) as a function of azimuthal angle. Polar plots of the PSS-polarized ESFG intensities of *n*-type (B) and *p*-type GaP(100) (D) as a function of azimuthal angle at an ESFG wavelength of 490 nm.

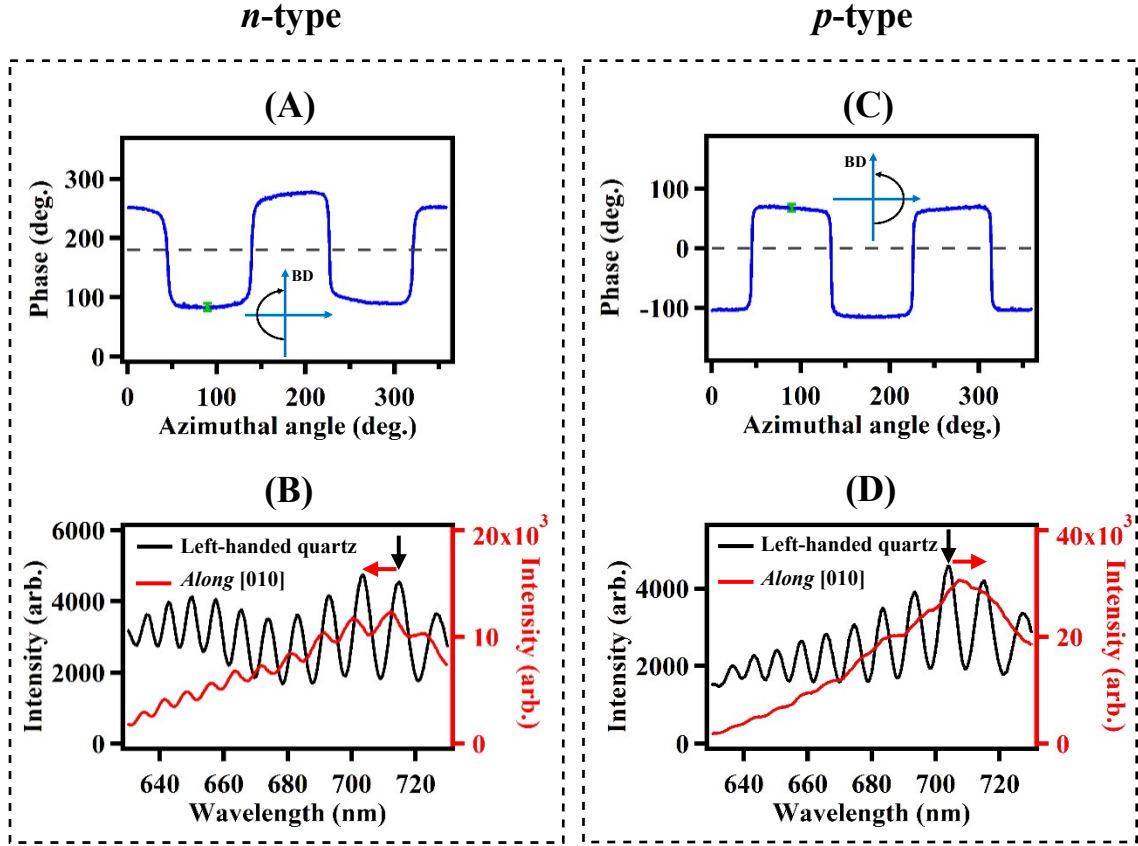


Figure 3. The absolute phases of *n*-type (A) and *p*-type (C) GaP(100) (S-in/P-out) as a function of azimuthal angle at 700 nm. The phase error (Green bar) was $\pm 6^\circ$. Interference ESHG spectra for *n*-type (B) and *p*-type (D) GaP(100) (S-in/P-out) along the surface-dominant [010] axes as compared with that for the left-handed z-cut α -quartz crystal along the $+X$ axis. In wavelength domain, phases lead for the *n*-type, while phases lag for the *p*-type, as shown in arrows (B&D).

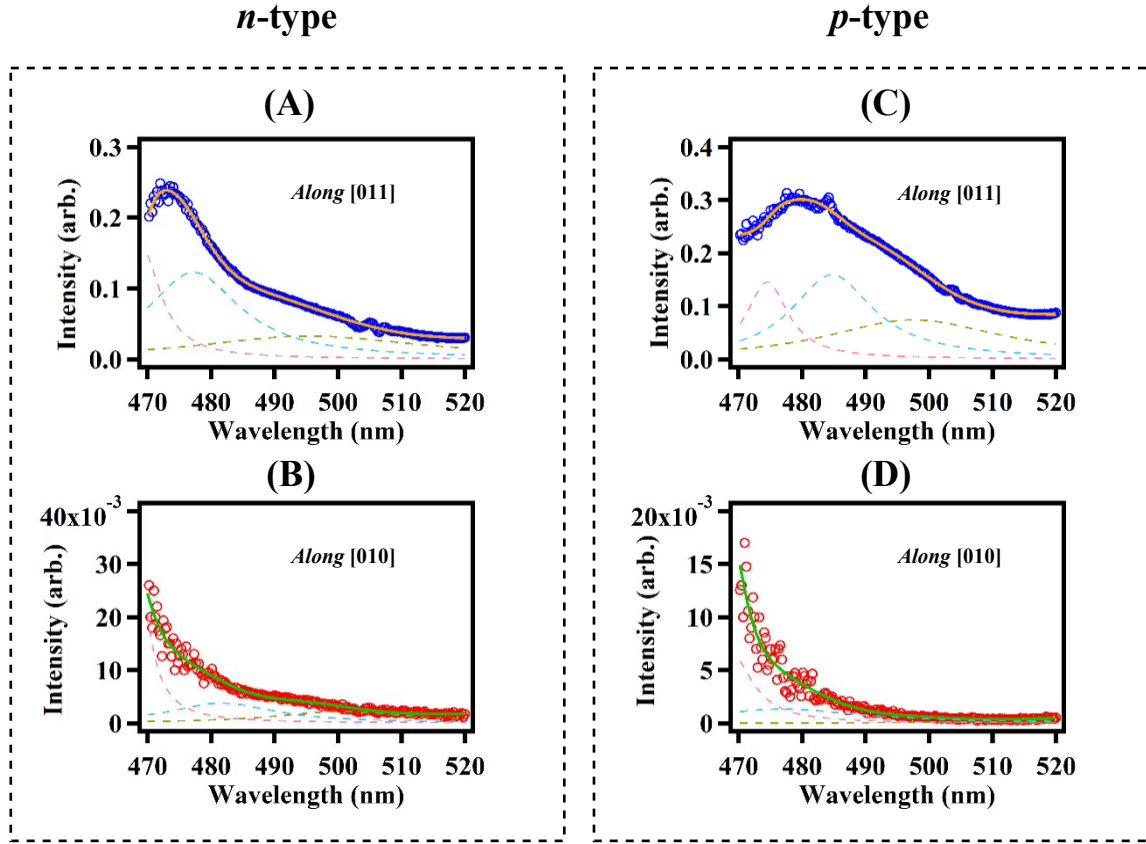


Figure 4. PSS-polarized ESFG spectra for *n*-type GaP(100) along the bulk-dominant [011] axis (A) and the surface-dominant [010] axis (B), as well as *p*-type GaP(100) along the bulk-dominant [011] axis (C) and surface-dominant [010] axis (D).

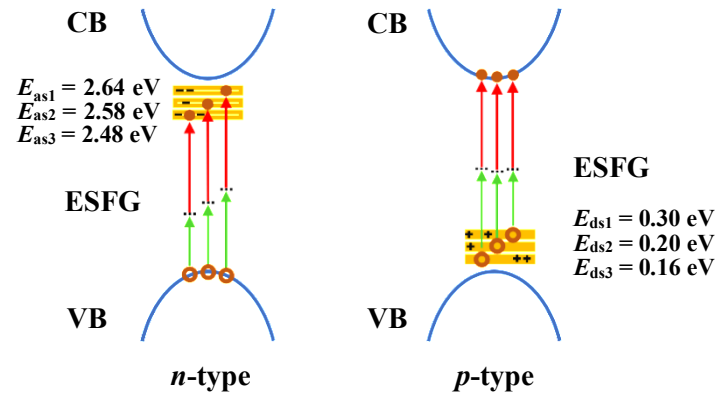


Figure 5. Schematic of energy levels for surface states of *n*-type (left) and *p*-type (right) GaP(100) crystals.

References

- (1) Ochedi, F. O.; Liu, D.; Yu, J.; Hussain, A.; Liu, Y. Photocatalytic, Electrocatalytic and Photoelectrocatalytic Conversion of Carbon Dioxide: A Review. *Environ. Chem. Lett.* **2021**, *19*, 941-967.
- (2) Ješić, D.; Lašić Jurković, D.; Pohar, A.; Suhadolnik, L.; Likozar, B. Engineering Photocatalytic and Photoelectrocatalytic CO₂ Reduction Reactions: Mechanisms, Intrinsic Kinetics, Mass Transfer Resistances, Reactors and Multi-Scale Modelling Simulations. *Chem. Eng. J.* **2021**, *407*, 126799.
- (3) Wang, G.; Pan, J.; Jiang, S. P.; Yang, H. Gas Phase Electrochemical Conversion of Humidified CO₂ to CO and H₂ on Proton-Exchange and Alkaline Anion-Exchange Membrane Fuel Cell Reactors. *J. CO₂ Util.* **2018**, *23*, 152-158.
- (4) Maeda, K. Metal-Complex/Semiconductor Hybrid Photocatalysts and Photoelectrodes for CO₂ Reduction Driven by Visible Light. *Adv. Mater.* **2019**, *31*, 1808205.
- (5) Song, J. T.; Ryoo, H.; Cho, M.; Kim, J.; Kim, J.-G.; Chung, S.-Y.; Oh, J. Nanoporous Au Thin Films on Si Photoelectrodes for Selective and Efficient Photoelectrochemical CO₂ Reduction. *Adv. Energy Mater.* **2017**, *7*, 1601103.
- (6) AlOtaibi, B.; Fan, S.; Wang, D.; Ye, J.; Mi, Z. Wafer-Level Artificial Photosynthesis for CO₂ Reduction into CH₄ and CO Using Ga Nanowires. *ACS Catal.* **2015**, *5*, 5342-5348.
- (7) Lin, W.; Han, H.; Frei, H. CO₂ Splitting by H₂O to CO and O₂ under UV Light in TiMCM-41 Silicate Sieve. *J. Phys. Chem. B* **2004**, *108*, 18269-18273.
- (8) Hinogami, R.; Nakamura, Y.; Yae, S.; Nakato, Y. Modification of Semiconductor Surface with Ultrafine Metal Particles for Efficient Photoelectrochemical Reduction of Carbon Dioxide. *Appl. Surf. Sci.* **1997**, *121-122*, 301-304.
- (9) Arai, T.; Sato, S.; Kajino, T.; Morikawa, T. Solar CO₂ Reduction Using H₂O by a Semiconductor/Metal-Complex Hybrid Photocatalyst: Enhanced Efficiency and Demonstration of a Wireless System Using SrTiO₃ Photoanodes. *Energy Environ. Sci.* **2013**, *6*, 1274-1282.
- (10) Halman, M. Photoelectrochemical Reduction of Aqueous Carbon Dioxide on p-Type Gallium Phosphide in Liquid Junction Solar Cells. *Nature* **1978**, *275*, 115-116.
- (11) Barton, E. E.; Rampulla, D. M.; Bocarsly, A. B. Selective Solar-Driven Reduction of CO₂ to Methanol Using a Catalyzed p-GaP Based Photoelectrochemical Cell. *J. Am. Chem. Soc.* **2008**, *130*, 6342-6344.
- (12) Schreier, M.; Luo, J.; Gao, P.; Moehl, T.; Mayer, M. T.; Grätzel, M. Covalent Immobilization of a Molecular Catalyst on Cu₂O Photocathodes for CO₂ Reduction. *J. Am. Chem. Soc.* **2016**, *138*, 1938-1946.
- (13) Pawar, A. U.; Kim, C. W.; Nguyen-Le, M.-T.; Kang, Y. S. General Review on the Components and Parameters of Photoelectrochemical System for CO₂ Reduction with in Situ Analysis. *ACS Sustainable Chem. Eng.* **2019**, *7*, 7431-7455.
- (14) Memming, R.; Tributsch, H. Electrochemical Investigations on the Spectral Sensitization of Gallium Phosphide Electrodes. *J. Phys. Chem.* **1971**, *75*, 562-570.
- (15) Tomkiewicz, M.; Woodall Jerry, M. Photoassisted Electrolysis of Water by Visible Irradiation of a p-Type Gallium Phosphide Electrode. *Science* **1977**, *196*, 990-991.
- (16) Malizia, M.; Seger, B.; Chorkendorff, I.; Vesborg, P. C. K. Formation of a P-N Heterojunction on GaP Photocathodes for H₂ Production Providing an Open-Circuit Voltage of 710 mV. *J. Mater. Chem. A* **2014**, *2*, 6847-6853.
- (17) Liu, C.; Sun, J.; Tang, J.; Yang, P. Zn-Doped p-Type Gallium Phosphide Nanowire Photocathodes from a Surfactant-Free Solution Synthesis. *Nano Lett.* **2012**, *12*, 5407-5411.
- (18) Hu, S.; Shaner Matthew, R.; Beardslee Joseph, A.; Lichterman, M.; Brunschwig Bruce, S.; Lewis Nathan, S. Amorphous TiO₂ Coatings Stabilize Si, GaAs, and GaP Photoanodes for Efficient Water Oxidation. *Science* **2014**, *344*, 1005-1009.

- (19) Nakato, Y.; Ohnishi, T.; Tsubomura, H. Photo-Electrochemical Behaviors of Semiconductor Electrodes Coated with Thin Metal Films. *Chem. Lett.* **1975**, *4*, 883-886.
- (20) Standing, A.; Assali, S.; Gao, L.; Verheijen, M. A.; van Dam, D.; Cui, Y.; Notten, P. H. L.; Haverkort, J. E. M.; Bakkers, E. P. A. M. Efficient Water Reduction with Gallium Phosphide Nanowires. *Nat. Commun.* **2015**, *6*, 7824.
- (21) Bagal, I. V.; Arunachalam, M.; Waseem, A.; Abdullah, A.; Kang, S. H.; Ryu, S.-W. Gallium Phosphide Photoanodes Coated with Nickel Oxyhydroxide Cocatalyst for Stable Photoelectrochemical Water Splitting Reactions. *Appl. Surf. Sci.* **2021**, *558*, 149873.
- (22) Ziegler, J.; Fertig, D.; Kaiser, B.; Jaegermann, W.; Blug, M.; Hoch, S.; Busse, J. Preparation and Characterization of GaP Semiconductor Electrodes for Photoelectrochemical Water Splitting. *Energy Procedia* **2012**, *22*, 108-113.
- (23) Lu, X.; Gao, X.; Li, C.; Ren, J.; Guo, X.; La, P. Electronic Structure and Optical Properties of Doped Gallium Phosphide: A First-Principles Simulation. *Phys. Lett. A* **2017**, *381*, 2986-2992.
- (24) Grinblat, G.; Nielsen Michael, P.; Dichtl, P.; Li, Y.; Oulton Rupert, F.; Maier Stefan, A. Ultrafast Sub-30-Fs All-Optical Switching Based on Gallium Phosphide. *Sci. Adv.* **2019**, *5*, eaaw3262.
- (25) Zeng, G.; Qiu, J.; Li, Z.; Pavaskar, P.; Cronin, S. B. CO₂ Reduction to Methanol on TiO₂-Passivated GaP Photocatalysts. *ACS Catal.* **2014**, *4*, 3512-3516.
- (26) Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. Photoelectrocatalytic Reduction of Carbon Dioxide in Aqueous Suspensions of Semiconductor Powders. *Nature* **1979**, *277*, 637-638.
- (27) Aurian-Blajeni, B.; Halmann, M.; Manassen, J. Electrochemical Measurement on the Photoelectrochemical Reduction of Aqueous Carbon Dioxide on p-Gallium Phosphide and p-Gallium Arsenide Semiconductor Electrodes. *Sol. Energy Mater.* **1983**, *8*, 425-440.
- (28) Xu, S.; Carter, E. A. CO₂ Photoelectrochemical Reduction Catalyzed by a GaP(001) Photoelectrode. *ACS Catal.* **2021**, *11*, 1233-1241.
- (29) Gupta, R.; Xiong, Q.; Mahan, G. D.; Eklund, P. C. Surface Optical Phonons in Gallium Phosphide Nanowires. *Nano Lett.* **2003**, *3*, 1745-1750.
- (30) Barker, A. S. Dielectric Dispersion and Phonon Line Shape in Gallium Phosphide. *Phys. Rev.* **1968**, *165*, 917-922.
- (31) Hsu, E. M.; Crawford, T. H. R.; Maunders, C.; Botton, G. A.; Haugen, H. K. Cross-Sectional Study of Periodic Surface Structures on Gallium Phosphide Induced by Ultrashort Laser Pulse Irradiation. *Appl. Phys. Lett.* **2008**, *92*, 221112.
- (32) Norman, D.; McGovern, I. T.; Norris, C. Surface States on Gallium Phosphide. *Phys. Lett. A* **1977**, *63*, 384-386.
- (33) Hamilton, B.; Peaker, A. R.; Wight, D. R. Deep-State-Controlled Minority-Carrier Lifetime in n-Type Gallium Phosphide. *J. Appl. Phys.* **1979**, *50*, 6373-6385.
- (34) Lubberhuizen, W. H.; Vanmaekelbergh, D.; Van Faassen, E. Recombination of Photogenerated Charge Carriers in Nanoporous Gallium Phosphide. *J. Porous Mater.* **2000**, *7*, 147-152.
- (35) Ichihashi, F.; Kawaguchi, T.; Dong, X.; Kuwahara, M.; Ito, T.; Harada, S.; Tagawa, M.; Ujihara, T. Temperature Dependence of Carrier Relaxation Time in Gallium Phosphide Evaluated by Photoemission Measurements. *AIP Adv.* **2017**, *7*, 115314.
- (36) Grinblat, G.; Zhang, H.; Nielsen Michael, P.; Krivitsky, L.; Berté, R.; Li, Y.; Tilmann, B.; Cortés, E.; Oulton Rupert, F.; Kuznetsov Arseniy, I.; et al. Efficient Ultrafast All-Optical Modulation in a Nonlinear Crystalline Gallium Phosphide Nanodisk at the Anapole Excitation. *Sci. Adv.* **2020**, *6*, eabb3123.
- (37) Szuber, J. Surface Photovoltage Spectroscopy Investigations of the Electronic Surface States on Clean and Oxygen-Exposed Polar GaAs(100) and GaAs(111) Surfaces. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *53*, 19-28.
- (38) Liehr, M.; Lüth, H. Gas Adsorption on Cleaved GaAs(110) Surfaces Studied by Surface Photovoltage Spectroscopy. *J. Vac. Sci. Technol.* **1979**, *16*, 1200-1206.

- (39) Szuber, J. Surface Photovoltage Spectroscopy Investigation of the Electronic Properties of a GaAs(100) Surface Thermally Cleaned in an Ultrahigh Vacuum and Subsequently Covered with Oxygen. *Thin Solid Films* **1984**, *112*, 309-312.
- (40) Adamowicz, B.; Szuber, J. Near-Band Gap Transitions in the Surface Photovoltage Spectra for GaAs, GaP and Si Surfaces. *Surf. Sci.* **1991**, *247*, 94-99.
- (41) Donchev, V.; Kirilov, K.; Ivanov, T.; Germanova, K. Surface Photovoltage Phase Spectroscopy – a Handy Tool for Characterisation of Bulk Semiconductors and Nanostructures. *Mater. Sci. Eng., B* **2006**, *129*, 186-192.
- (42) Straub, D.; Dose, V.; Altmann, W. Investigation of Intrinsic Unoccupied Surface States at GaP(110) by Inverse Photoemission. *Surf. Sci.* **1983**, *133*, 9-14.
- (43) Ramakrishna, S.; Willig, F.; Knorr, A. Photoinduced Bulk-Surface Dynamics: Time Resolved Two Photon Photoemission Signals at Semiconductor Surfaces. *Surf. Sci.* **2004**, *558*, 159-173.
- (44) Bokor, J.; Halas, N. J. Time-Resolved Study of Silicon Surface Recombination. *IEEE J. Quantum Electron.* **1989**, *25*, 2550-2555.
- (45) Mauerer, M.; Shumay, I. L.; Berthold, W.; Höfer, U. Ultrafast Carrier Dynamics in Si(111)7x7 Dangling Bonds Probed by Time-Resolved Second-Harmonic Generation and Two-Photon Photoemission. *Phys. Rev. B* **2006**, *73*, 245305.
- (46) Zhang, Z.; Yates Jr, J. T. Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces. *Chem. Rev.* **2012**, *112*, 5520-5551.
- (47) Lüth, H. In *Solid Surfaces, Interfaces and Thin Films*; Lüth, H., Ed.; Springer: Berlin, 2015; Vol. 6, pp 253-335.
- (48) Lüth, H. *Solid Surfaces, Interfaces and Thin Films*; Springer: Berlin, 2015.
- (49) Spindt, C. J.; Spicer, W. E. Sulfur Passivation of Gaas Surfaces: A Model for Reduced Surface Recombination without Band Flattening. *Appl. Phys. Lett.* **1989**, *55*, 1653-1655.
- (50) Cortes-Mestizo, I. E.; Briones, E.; Espinosa-Vega, L. I.; Mendez-Garcia, V. H. In *Electromagnetic Materials and Devices*; Han, M., Ed.; IntechOpen: London, 2020; Vol. 15, p. 86469.
- (51) Shen, Y. R. Surface Properties Probed by Second-Harmonic and Sum-Frequency Generation. *Nature* **1989**, *337*, 519-525.
- (52) Eienthal, K. B. Photochemistry and Photophysics of Liquid Interfaces by Second Harmonic Spectroscopy. *J. Phys. Chem.* **1996**, *100*, 12997-13006.
- (53) Eienthal, K. B. Liquid Interfaces Probed by Second-Harmonic and Sum-Frequency Spectroscopy. *Chem. Rev.* **1996**, *96*, 1343-1360.
- (54) Miranda, P. B.; Shen, Y. R. Liquid Interfaces: A Study by Sum-Frequency Vibrational Spectroscopy. *J. Phys. Chem. B* **1999**, *103*, 3292-3307.
- (55) Chen, Z.; Shen, Y.; Somorjai, G. A. Studies of Polymer Surfaces by Sum Frequency Generation Vibrational Spectroscopy. *Annu. Rev. Phys. Chem.* **2002**, *53*, 437-465.
- (56) Richmond, G. L. Molecular Bonding and Interactions at Aqueous Surfaces as Probed by Vibrational Sum Frequency Spectroscopy. *Chem. Rev.* **2002**, *102*, 2693-2724.
- (57) Wang, H. F.; Gan, W.; Lu, R.; Rao, Y.; Wu, B. H. Quantitative Spectral and Orientational Analysis in Surface Sum Frequency Generation Vibrational Spectroscopy (SFG-VS). *Int. Rev. Phys. Chem.* **2005**, *24*, 191-256.
- (58) Geiger, F. M. Second Harmonic Generation, Sum Frequency Generation, and $\chi^{(2)}$: Dissecting Environmental Interfaces with a Nonlinear Optical Swiss Army Knife. *Annu. Rev. Phys. Chem.* **2009**, *60*, 61-83.
- (59) Arnolds, H.; Bonn, M. Ultrafast Surface Vibrational Dynamics. *Surf. Sci. Rep.* **2010**, *65*, 45-66.
- (60) Jubb, A. M.; Hua, W.; Allen, H. C. Environmental Chemistry at Vapor/Water Interfaces: Insights from Vibrational Sum Frequency Generation Spectroscopy. *Annu. Rev. Phys. Chem.* **2012**, *63*, 107-130.

- (61) Johnson, C. M.; Baldelli, S. Vibrational Sum Frequency Spectroscopy Studies of the Influence of Solutes and Phospholipids at Vapor/Water Interfaces Relevant to Biological and Environmental Systems. *Chem. Rev.* **2014**, *114*, 8416-8446.
- (62) Yan, E. C. Y.; Fu, L.; Wang, Z. G.; Liu, W. Biological Macromolecules at Interfaces Probed by Chiral Vibrational Sum Frequency Generation Spectroscopy. *Chem. Rev.* **2014**, *114*, 8471-8498.
- (63) Berne, B. J.; Fourkas, J. T.; Walker, R. A.; Weeks, J. D. Nitriles at Silica Interfaces Resemble Supported Lipid Bilayers. *Acc. Chem. Res.* **2016**, *49*, 1605-1613.
- (64) Elsenbeck, D.; Das, S. K.; Velarde, L. Substrate Influence on the Interlayer Electron-Phonon Couplings in Fullerene Films Probed with Doubly-Resonant SFG Spectroscopy. *Phys. Chem. Chem. Phys.* **2017**, *19*, 18519-18528.
- (65) Velarde, L.; Zhang, X. Y.; Lu, Z.; Joly, A. G.; Wang, Z. M.; Wang, H. F. Communication: Spectroscopic Phase and Lineshapes in High-Resolution Broadband Sum Frequency Vibrational Spectroscopy: Resolving Interfacial Inhomogeneities of "Identical" Molecular Groups. *J. Chem. Phys.* **2011**, *135*, 241102.
- (66) Stiopkin, I. V.; Weeraman, C.; Pieniazek, P. A.; Shalhout, F. Y.; Skinner, J. L.; Benderskii, A. V. Hydrogen Bonding at the Water Surface Revealed by Isotopic Dilution Spectroscopy. *Nature* **2011**, *474*, 192-195.
- (67) Liu, W.-T.; Shen, Y. R. In Situ Sum-Frequency Vibrational Spectroscopy of Electrochemical Interfaces with Surface Plasmon Resonance. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 1293.
- (68) Qian, Y.; Deng, G.-h.; Rao, Y. In Situ Spectroscopic Probing of Polarity and Molecular Configuration at Aerosol Particle Surfaces. *J. Phys. Chem. Lett.* **2020**, *11*, 6763-6771.
- (69) Mizuno, H.; Rizzuto, A. M.; Saykally, R. J. Charge-Transfer-to-Solvent Spectrum of Thiocyanate at the Air/Water Interface Measured by Broadband Deep Ultraviolet Electronic Sum Frequency Generation Spectroscopy. *J. Phys. Chem. Lett.* **2018**, *9*, 4753-4757.
- (70) Deng, G.-H.; Qian, Y.; Rao, Y. Development of Ultrafast Broadband Electronic Sum Frequency Generation for Charge Dynamics at Surfaces and Interfaces. *J. Chem. Phys.* **2019**, *150*, 024708.
- (71) Deng, G.-H.; Qian, Y.; Wei, Q.; Zhang, T.; Rao, Y. Interface-Specific Two-Dimensional Electronic Sum Frequency Generation Spectroscopy. *J. Phys. Chem. Lett.* **2020**, *11*, 1738-1745.
- (72) Sekiguchi, K.; Yamaguchi, S.; Tahara, T. Femtosecond Time-Resolved Electronic Sum-Frequency Generation Spectroscopy: A New Method to Investigate Ultrafast Dynamics at Liquid Interfaces. *J. Chem. Phys.* **2008**, *128*, 114715.
- (73) Moon, A. P.; Pandey, R.; Bender, J. A.; Cotton, D. E.; Renard, B. A.; Roberts, S. T. Using Heterodyne-Detected Electronic Sum Frequency Generation to Probe the Electronic Structure of Buried Interfaces. *J. Phys. Chem. C* **2017**, *121*, 18653-18664.
- (74) Li, Y. M.; Wang, J. M.; Xiong, W. Probing Electronic Structures of Organic Semiconductors at Buried Interfaces by Electronic Sum Frequency Generation Spectroscopy. *J. Phys. Chem. C* **2015**, *119*, 28083-28089.
- (75) Yamaguchi, S.; Tahara, T. Precise Electronic $\chi^{(\#)}$ Spectra of Molecules Adsorbed at an Interface Measured by Multiplex Sum Frequency Generation. *J. Phys. Chem. B* **2004**, *108*, 19079-19082.
- (76) Watson, B. R.; Doughty, B.; Calhoun, T. R. Energetics at the Surface: Direct Optical Mapping of Core and Surface Electronic Structure in CdSe Quantum Dots Using Broadband Electronic Sum Frequency Generation Microspectroscopy. *Nano Lett.* **2019**, *19*, 6157-6165.
- (77) Cotton, D. E.; Moon, A. P.; Roberts, S. T. Using Electronic Sum-Frequency Generation to Analyze the Interfacial Structure of Singlet Fission-Capable Perylenediimide Thin Films. *J. Phys. Chem. C* **2020**, *124*, 11401-11413.
- (78) Takahashi, H.; Watanabe, R.; Miyauchi, Y.; Mizutani, G. Discovery of Deep and Shallow Trap States from Step Structures of Rutile TiO₂ Vicinal Surfaces by Second Harmonic and Sum Frequency Generation Spectroscopy. *J. Chem. Phys.* **2011**, *134*, 154704.
- (79) Roke, S.; Roeterdink, W. G.; Wijnhoven, J. E.; Petukhov, A. V.; Kleyn, A. W.; Bonn, M. Vibrational Sum Frequency Scattering from a Submicron Suspension. *Phys. Rev. Lett.* **2003**, *91*, 258302.

- (80) Wang, C. Y.; Groenzin, H.; Shultz, M. J. Surface Characterization of Nanoscale TiO₂ Film by Sum Frequency Generation Using Methanol as a Molecular Probe. *J. Phys. Chem. B* **2004**, *108*, 265-272.
- (81) Kung, K. Y.; Chen, P.; Wei, F.; Shen, Y. R.; Somorjai, G. A. Sum-Frequency Generation Spectroscopic Study of Co Adsorption and Dissociation on Pt(111) at High Pressure and Temperature. *Surf. Sci.* **2000**, *463*, L627-L633.
- (82) Makarem, M.; Lee, C. M.; Sawada, D.; O'Neill, H. M.; Kim, S. H. Distinguishing Surface Versus Bulk Hydroxyl Groups of Cellulose Nanocrystals Using Vibrational Sum Frequency Generation Spectroscopy. *J. Phys. Chem. Lett.* **2017**, *9*, 70-75.
- (83) Vanselow, H.; Stingel, A. M.; Petersen, P. B. Interferometric 2D Sum Frequency Generation Spectroscopy Reveals Structural Heterogeneity of Catalytic Monolayers on Transparent Materials. *J. Phys. Chem. Lett.* **2017**, *8*, 825-830.
- (84) Wang, H. Y.; Gao, T.; Xiong, W. Self-Phase-Stabilized Heterodyne Vibrational Sum Frequency Generation Microscopy. *ACS Photonics* **2017**, *4*, 1839-1845.
- (85) Laaser, J. E.; Zanni, M. T. Extracting Structural Information from the Polarization Dependence of One- and Two-Dimensional Sum Frequency Generation Spectra. *J. Phys. Chem. A* **2013**, *117*, 5875-5890.
- (86) Liljeblad, J. F.; Tyrode, E. Vibrational Sum Frequency Spectroscopy Studies at Solid/Liquid Interfaces: Influence of the Experimental Geometry in the Spectral Shape and Enhancement. *J. Phys. Chem. C* **2012**, *116*, 22893-22903.
- (87) Chowdhury, A. U.; Liu, F.; Watson, B. R.; Ashkar, R.; Katsaras, J.; Patrick Collier, C.; Lutterman, D. A.; Ma, Y.-Z.; Calhoun, T. R.; Doughty, B. Flexible Approach to Vibrational Sum-Frequency Generation Using Shaped Near-Infrared Light. *Opt. Lett.* **2018**, *43*, 2038-2041.
- (88) Rey, N. G.; Dlott, D. D. Studies of Electrochemical Interfaces by Broadband Sum Frequency Generation. *J. Electroanal. Chem.* **2017**, *800*, 114-125.
- (89) Anglin, T. C.; Conboy, J. C. Kinetics and Thermodynamics of Flip-Flop in Binary Phospholipid Membranes Measured by Sum-Frequency Vibrational Spectroscopy. *Biochemistry* **2009**, *48*, 10220-10234.
- (90) Wen, Y.-C.; Zha, S.; Liu, X.; Yang, S.; Guo, P.; Shi, G.; Fang, H.; Shen, Y. R.; Tian, C. Unveiling Microscopic Structures of Charged Water Interfaces by Surface-Specific Vibrational Spectroscopy. *Phys. Rev. Lett.* **2016**, *116*, 016101.
- (91) Feng, R.-J.; Lin, L.; Li, Y.-Y.; Liu, M.-H.; Guo, Y.; Zhang, Z. Effect of Ca²⁺ to Sphingomyelin Investigated by Sum Frequency Generation Vibrational Spectroscopy. *Biophys. J.* **2017**, *112*, 2173-2183.
- (92) Liu, S.; Liu, A.-a.; Wen, B.; Zhang, R.; Zhou, C.; Liu, L.-M.; Ren, Z. Coverage Dependence of Methanol Dissociation on TiO₂ (110). *J. Phys. Chem. Lett.* **2015**, *6*, 3327-3334.
- (93) Xu, B.; Wu, Y.; Sun, D.; Dai, H.-L.; Rao, Y. Stabilized Phase Detection of Heterodyne Sum Frequency Generation for Interfacial Studies. *Opt. Lett.* **2015**, *40*, 4472-4475.
- (94) Germer, T. A.; Kolasin-acuteski, K. W.; Stephenson, J. C.; Richter, L. J. Depletion-Electric-Field-Induced Second-Harmonic Generation near Oxidized GaAs(001) Surfaces. *Phys. Rev. B* **1997**, *55*, 10694-10706.
- (95) Yamada, C.; Kimura, T. Anisotropy in Second-Harmonic Generation from Reconstructed Surfaces of GaAs. *Phys. Rev. Lett.* **1993**, *70*, 2344-2347.
- (96) Armstrong, S. R.; Hoare, R. D.; Pemble, M. E.; Povey, I. M.; Stafford, A.; Taylor, A. G. Optical Second Harmonic Generation Studies of the Nature of the GaAs(100) Surface in Air. *J. Cryst. Growth* **1992**, *120*, 94-97.
- (97) Ponath, H.-E.; Stegeman, G. I. *Nonlinear Surface Electromagnetic Phenomena*; Elsevier: Amsterdam, 2012.
- (98) Thämer, M.; Garling, T.; Campen, R. K.; Wolf, M. Quantitative Determination of the Nonlinear Bulk and Surface Response from Alpha-Quartz Using Phase Sensitive SFG Spectroscopy. *J. Chem. Phys.* **2019**, *151*, 064707.
- (99) de Beer, A. G. F.; Campen, R. K.; Roke, S. Separating Surface Structure and Surface Charge with Second-Harmonic and Sum-Frequency Scattering. *Phys. Rev. B* **2010**, *82*, 235431.

- (100) Wang, F. X.; Rodríguez, F. J.; Albers, W. M.; Ahorinta, R.; Sipe, J. E.; Kauranen, M. Surface and Bulk Contributions to the Second-Order Nonlinear Optical Response of a Gold Film. *Phys. Rev. B* **2009**, *80*, 233402.
- (101) Deckoff-Jones, S.; Zhang, J.; Petoukhoff, C. E.; Man, M. K. L.; Lei, S.; Vajtai, R.; Ajayan, P. M.; Talbayev, D.; Madéo, J.; Dani, K. M. Observing the Interplay between Surface and Bulk Optical Nonlinearities in Thin Van Der Waals Crystals. *Sci. Rep.* **2016**, *6*, 22620.
- (102) Park, H.; Gutierrez, M.; Wu, X.; Kim, W.; Zhu, X.-Y. Optical Probe of Charge Separation at Organic/Inorganic Semiconductor Interfaces. *J. Phys. Chem. C* **2013**, *117*, 10974-10979.
- (103) Tisdale, W. A.; Williams, K. J.; Timp, B. A.; Norris, D. J.; Aydil, E. S.; Zhu, X.-Y. Hot-Electron Transfer from Semiconductor Nanocrystals. *Science* **2010**, *328*, 1543-1547.
- (104) Nelson, C.; Luo, J.; Jen, A.-Y.; Laghumavarapu, R.; Huffaker, D.; Zhu, X.-Y. Time-, Energy-, and Phase-Resolved Second-Harmonic Generation at Semiconductor Interfaces. *J. Phys. Chem. C* **2014**, *118*, 27981-27988.
- (105) Zhang, Z.; Kim, J.; Khoury, R.; Saghayezhian, M.; Haber, L. H.; Plummer, E. Surface Sum Frequency Generation Spectroscopy on Non-Centrosymmetric Crystal GaAs (001). *Surf. Sci.* **2017**, *664*, 21-28.
- (106) Tom, H. W. K.; Heinz, T. F.; Shen, Y. R. Second-Harmonic Reflection from Silicon Surfaces and Its Relation to Structural Symmetry. *Phys. Rev. Lett.* **1983**, *51*, 1983-1986.
- (107) Liu, Y.; Dadap, J. I.; Zimdars, D.; Eienthal, K. B. Study of Interfacial Charge-Transfer Complex on TiO₂ Particles in Aqueous Suspension by Second-Harmonic Generation. *J. Phys. Chem. B* **1999**, *103*, 2480-2486.
- (108) Mund, J.; Uihlein, C.; Fröhlich, D.; Yakovlev, D. R.; Bayer, M. Second Harmonic Generation on the Yellow 1s Exciton in Cu₂O in Symmetry-Forbidden Geometries. *Phys. Rev. B* **2019**, *99*, 195204.
- (109) Janner, A. M.; Eder, R.; Koopmans, B.; Jonkman, H. T.; Sawatzky, G. A. Excitons in C₆₀ Studied by Temperature-Dependent Optical Second-Harmonic Generation. *Phys. Rev. B* **1995**, *52*, 17158-17164.
- (110) Daum, W.; Krause, H. J.; Reichel, U.; Ibach, H. Nonlinear Optical Spectroscopy at Silicon Interfaces. *Phys. Scr.* **1993**, *T49B*, 513-518.
- (111) Yamada, C.; Kimura, T. Rotational Symmetry of the Surface Second-Harmonic Generation of Zinc-Blende-Type Crystals. *Phys. Rev. B* **1994**, *49*, 14372-14381.
- (112) Rommel, P.; Main, J.; Farenbruch, A.; Mund, J.; Fröhlich, D.; Yakovlev, D. R.; Bayer, M.; Uihlein, C. Second Harmonic Generation of Cuprous Oxide in Magnetic Fields. *Phys. Rev. B* **2020**, *101*, 115202.
- (113) Mund, J.; Fröhlich, D.; Yakovlev, D. R.; Bayer, M. High-Resolution Second Harmonic Generation Spectroscopy with Femtosecond Laser Pulses on Excitons in Cu₂O. *Phys. Rev. B* **2018**, *98*, 085203.
- (114) Farenbruch, A.; Mund, J.; Fröhlich, D.; Yakovlev, D. R.; Bayer, M.; Semina, M. A.; Glazov, M. M. Magneto-Stark and Zeeman Effect as Origin of Second Harmonic Generation of Excitons in Cu₂O. *Phys. Rev. B* **2020**, *101*, 115201.
- (115) Shen, Y. R. Optical Second Harmonic Generation at Interfaces. *Annu. Rev. Phys. Chem.* **1989**, *40*, 327-350.
- (116) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.
- (117) Shen, Y. R. *Fundamentals of Sum-Frequency Spectroscopy*; Cambridge University Press: Cambridge, U.K., 2016.
- (118) Bloembergen, N. *Nonlinear Optics : A Lecture Note and Reprint Volume*; W.A. Benjamin: New York, 1965.
- (119) Butcher, P. N.; Cotter, D. *The Elements of Nonlinear Optics*; Cambridge University Press: Cambridge, U.K., 1990.
- (120) Zhuang, X.; Miranda, P. B.; Kim, D.; Shen, Y. R. Mapping Molecular Orientation and Conformation at Interfaces by Surface Nonlinear Optics. *Phys. Rev. B* **1999**, *59*, 12632-12640.
- (121) Boyd, R. W. *Nonlinear Optics: Third Edition*; Academic: Burlington, 2008.

- (122) Wei, X.; Hong, S.-C.; Lvovsky, A. I.; Held, H.; Shen, Y. R. Evaluation of Surface vs Bulk Contributions in Sum-Frequency Vibrational Spectroscopy Using Reflection and Transmission Geometries. *J. Phys. Chem. B* **2000**, *104*, 3349-3354.
- (123) Ohno, P. E.; Wang, H.-f.; Geiger, F. M. Second-Order Spectral Lineshapes from Charged Interfaces. *Nat. Commun.* **2017**, *8*, 1032.
- (124) Ohno, P. E.; Saslow, S. A.; Wang, H.-f.; Geiger, F. M.; Eienthal, K. B. Phase-Referenced Nonlinear Spectroscopy of the α -Quartz/Water Interface. *Nat. Commun.* **2016**, *7*, 13587, Article.
- (125) Rao, Y.; Kwok, S. J. J.; Lombardi, J.; Turro, N. J.; Eienthal, K. B. Label-Free Probe of HIV-1 TAT Peptide Binding to Mimetic Membranes. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 12684.
- (126) Wang, H.; Hu, X.-H.; Wang, H.-F. Charge-Induced $\chi^{(3)}$ Susceptibility in Interfacial Nonlinear Optical Spectroscopy Beyond the Bulk Aqueous Contributions: The Case for Silica/Water Interface. *J. Phys. Chem. C* **2021**, *125*, 26208-26215.
- (127) Villaeys, A. A.; Pflumio, V.; Lin, S. H. Theory of Second-Harmonic Generation of Molecular Systems: The Case of Coincident Pulses. *Phys. Rev. A* **1994**, *49*, 4996-5014.
- (128) Deng, G.-H.; Wei, Q.; Qian, Y.; Zhang, T.; Leng, X.; Rao, Y. Development of Interface-/Surface-Specific Two-Dimensional Electronic Spectroscopy. *Rev. Sci. Instrum.* **2021**, *92*, 023104.
- (129) Zhang, T.; Huangfu, Z.; Qian, Y.; Lu, Z.; Gao, H.; Rao, Y. Spectral Phase Measurements of Heterodyne Detection in Interfacial Broadband Electronic Spectroscopy. *J. Phys. Chem. C* **2022**, *126*, 2823-2832.
- (130) Yamaguchi, S.; Tahara, T. Heterodyne-Detected Electronic Sum Frequency Generation: “Up” Versus “Down” Alignment of Interfacial Molecules. *J. Chem. Phys.* **2008**, *129*, 101102.
- (131) Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. Direct Evidence for Orientational Flip-Flop of Water Molecules at Charged Interfaces: A Heterodyne-Detected Vibrational Sum Frequency Generation Study. *J. Chem. Phys.* **2009**, *130*, 204704.
- (132) Uchida, H.; Yoneyama, H.; Tamura, H. Surface States Formation Due to Impregnated Hydrogen at p-Type Gallium Phosphide Electrodes with Metal Adatoms. *J. Electrochem. Soc.* **1980**, *127*, 99-104.

TOC Graphic

