The nature of a nonlinear excitation pathway from the Shockley surface state as probed by chirped pulse two photon photoemission

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Abstract. Phase-modulated femtosecond laser pulses are used to study the spectral response of a non-resonant two photon excitation from the Cu(111) Shockley surface state (SS). Controlled variations in the spectral phase of the laser pulse were introduced using a tuneable Fork prism phase modulator and resulted in a shift in the peak-position (of up to 110 meV), variations in the spectral width (up to 88 meV) and changes in the asymmetry of the SS peak as detected by two-photon photoemission. A satisfactory quantitative model of the experimental results can only be achieved if the complete spectral phase up to the third-order dispersion terms is taken into account. Of particular note, we find that a consistent description of this two photon absorption process does not require coupling of the excitation to an intermediate copper bulk state, which contradicts the previous results of Petek \textit{et al} (1997 \textit{Phys. Rev. Lett.} \textbf{79} 4649).
1. Introduction

Two photon absorption processes are of paramount importance for the study and control of optical and electronic responses for a wide range of processes in the gas phase [1]–[3] as well as in condensed matter [4]–[8] and surface physics [9]–[14]. A quantitative and complete interpretation of these experiments requires a thorough knowledge of the processes determining this nonlinear light–matter interaction [15]. In the case of an isolated atom or molecule, this means taking into account the interaction of the light field with a multitude of discrete and well-separated electronic states [16]. Due to the formation of continuous electronic bands, this situation is made much more complex for a semiconductor or metal [11]. In addition, solid surfaces exhibit an even more complex electronic structure [10, 17, 18]. For example, in many cases, surface localized two-dimensional electronic states appear [9], which are more or less strongly coupled to the underlying three-dimensional substrate background. A two-photon excitation process involving surface localized states may, therefore, be strongly affected by its interaction with the electronic band structure of the bulk.

A prominent model surface system, which is characterized by a series of surface localized states, is the (111) oriented surface of a copper single crystal (see figure 1). It exhibits an occupied Shockley SS just below the Fermi-level (see red line in figure 1) as well as a Rydberg-like series of unoccupied image potential states and resonances that are bound below the vacuum level. Previously, second harmonic generation (SHG) and two photon photo-emission (2PPE) spectroscopy have been successfully applied to study the peculiarities of the electronic structure of the Cu(111) surface [19, 20], the population decay of image potential state excitations [21]–[23] or the resonant (Shockley state) mediated excitation of discrete adsorbate resonances [24]–[26].

In addition, the role of bulk electronic states within a non-resonant two-photon excitation process from the Shockley SS, as indicated by the blue arrows in figure 1, has been addressed by Petek et al [27] in a sophisticated 2PPE experiment using chirped femtosecond laser pulses in a 2PPE study. Their results indicated that the coupling of the laser excitation to the bulk electron background considerably affects the induced nonlinear response of the system as probed by the 2PPE. A phase-dependent spectral shift in the 2PPE signal from the Shockley SS could only be
Figure 1. Electronic structure of the Cu(111) surface in the vicinity of the Fermi-level. The white area corresponds to the surface L-gap extending at the Γ-point ($k_\parallel = 0 \text{ Å}^{-1}$) from $-0.85 \text{ eV}$ to $+4.5 \text{ eV}$ at room temperature with respect to the Fermi level $E_F$. The dispersive Shockley surface state (SS, red line) exhibits its minimum at a binding energy of $-390 \text{ meV}$. For the Cu(111) surface, only the $n = 1$ image potential state (IS) is located within the L-gap of the crystal. Higher order image potential states in the vicinity of the vacuum level are not shown. In the viewpoint, the non-resonant two-photon photo excitation pathway from the Shockley SS using light pulses with a wavelength of 399 nm is indicated by the blue arrows.

reproduced by a model that involves a real bulk electronic state in the intermediate step of the excitation [27].

In this work, we show that the involvement of a real intermediate bulk state is not required to account for these experimental findings. On the contrary, complete quantitative agreement between experiment and theory is achieved using a model that describes the excitation scenario according to a non-resonant second harmonic-like (SH-like) process. This model takes into account the phase terms of both second-order (group velocity dispersion (GVD)) and third-order (third-order dispersion (TOD)) phase modulated laser pulses. Furthermore, we find that the chirped pulses not only induce a spectral shift in the Shockley SS peak, but also lead to spectral broadening and spectral asymmetry. These experimental results are also almost perfectly reproduced by the applied model.

In addition to the spectral phase of a laser pulse, the detailed shape of the envelope of a transform-limited (flat-phase) laser pulse can also critically influence the spectral response mapped in 2PPE [28]. Please note that the latter issue will not be addressed in this paper.

2. Experimental setup

Figure 2 shows the experimental setup used for our 2PPE study with phase-modulated (chirped) laser pulses (hereafter referred to as ‘chirped pulse 2PPE’ (CP-2PPE)). The laser system consists

\footnote{The term ‘chirp’ used throughout this paper denotes a general phase modulation.}
Figure 2. Experimental scheme used for the CP-2PPE measurements. After frequency doubling in a beta barium borate (BBO) crystal, the GVD and TOD of the ultrafast laser pulses at 399 nm is adjusted by a Fork prism pair by translation of the first prism, as indicated by the green arrow. The chirped pulses are focused onto the Cu(111) sample within a ultra high vacuum (UHV) chamber. The photoemitted electrons are detected in a 2d hemispherical electron energy analyser.

of a mode-locked Ti:sapphire laser, pumped by 7.5 W from a diode pumped all-solid state laser. It delivers linearly-polarized, transform-limited pulses at a centre wavelength of 795 nm and a spectral width of 46 nm full-width at half-maximum (FWHM). This light is then frequency doubled in BBO crystals to 399 nm, equivalent to a photon energy of 3.11 eV. For these experiments, we used two different BBO crystals, one that was 100 µm thick and one that was 200 µm thick. The 100 µm BBO crystal produced pulses with a bandwidth of 11.9 nm (FWHM), supporting a 20 fs transform-limited pulse duration (hereafter referred to as ‘11.9 nm data’) whereas the 200 µm thick crystal produced 8.7 nm bandwidth, supporting a 27 fs pulse duration (‘8.7 nm data’). The spectral phase of the 399 nm femtosecond laser pulses is tuned by the translation of the first of both prisms within a Fork prism pair [29, 30] setup as illustrated in figure 2 (prism apex angle 68.7°). This scheme can be considered as a single-parameter phase modulator that allows a defined control over the degree of second-order spectral phase (GVD) of the pulses, and simultaneously changes the amount of TOD as well [31]. Both the spectral amplitude and the central wavelength of the 399 nm pulses are unaffected by this prism translation. The separation between the two prisms was adjusted to ensure that the pulses had a zero net-GVD at the sample position when the beam passed close to the centre of the adjustable prism. We refer to this adjustment as the ‘zero-position’ of the tuning prism. This procedure resulted in a separation between the two prisms of 41 cm and 51 cm for the 11.9 nm and 8.7 nm bandwidth pulses, respectively. Using this method, an equal range of positive and
Figure 3. CP-2PPE measurements for \( \text{GVD} = +441 \text{fs}^2 \) and \( \text{GVD} = 0 \text{fs}^2 \).
(a) Comparison of two 2PPE \( E(k_{\parallel}) \) intensity maps recorded with the hemispherical analyzer for two different chirp parameters (left: \( \text{GVD} = 441 \text{fs}^2 \), right: \( \text{GVD} = 0 \text{fs}^2 \)). Both measurements have been scaled separately, the 2PPE intensity increases from red and green to blue. (b) The corresponding, normalized energy distribution curves (EDCs; black line: \( \text{GVD} = 0 \text{fs}^2 \), red line: \( \text{GVD} = +441 \text{fs}^2 \)). The EDCs have been extracted by angular integration from \(-2^\circ\) to \(+2^\circ\) emission angle. A clear shift in the Shockley surface state (SS) energy by 55 meV is observed. Furthermore, the larger of the two GVD chirp values gives rise to a clear peak broadening by 25% corresponding to 56 meV, and a decrease in the 2PPE amplitude. For clarity, the data have been normalized to the Shockley state intensity maximum.

Negative GVD values (up to \( \pm 1500 \text{fs}^2 \)) are accessible in the CP-2PPE experiments. The change in spectral phase applied to the pulses by the prism translation, \( \Delta \phi \), is calculated using the Sellmeier [32] coefficients of the prism material (Suprasil) [33]–[35]. In addition, it is important to quantitatively account for the amount and change of the TOD of the pulses in the model to describe the experimental results. For example, a 10 mm thick piece of fused silica glass will introduce additional \( \text{GVD} = +976 \text{fs}^2 \) and \( \text{TOD} = +303 \text{fs}^3 \) from material dispersion. This will increase the duration of a transform-limited 20 fs pulse to 139 fs.

Angle-resolved 2PPE spectra from the Cu(111) surface using these phase-modulated pulses are recorded in an ultrahigh vacuum chamber equipped with a 150 mm hemispherical energy analyser (SPECS Phoibos 150). At the settings used in these experiments, this analyser has an energy resolution of 20 meV and an angular resolution of 0.15°. The detection unit consists of a microchannel plate, a phosphor screen and a CCD camera that allows for parallel detection of photoelectrons with emission angles up to \( \pm 7^\circ \) without sample rotation (see figure 3). For data analysis, the 2PPE spectra have been integrated over an emission angle range between \( \pm 2^\circ \) at around \( k_{\parallel} = 0 \text{Å}^{-1} \).

Prior to the experiments, the Cu(111) sample had been cleaned by successive sputtering (up to 10 min at 0.5–1.0 kV) and annealing (15 min, max 750 K) cycles. The surface quality of the
crystal was checked by low energy electron diffraction (LEED) and by the 2PPE characteristics (energy and spectral widths) of the Shockley SS of the Cu(111) surface. Please note that, for these reference measurements, an alternative, narrow-band Ti:sapphire laser system was used. All measurements were performed at room temperature.

In the CP-2PPE experiments, we recorded spectra as a function of the phase modulation applied to the femtosecond laser pulses by the tuneable Fork prism pair setup. The effect of the chirp variation on the measured 2PPE spectrum is illustrated in figure 3(a), which shows a $E(k_{\parallel})$ 2PPE intensity map for a GVD of 441 fs$^2$ (left side) compared to an intensity map with vanishing GVD (right side). The corresponding normalized 2PPE energy distribution curves (EDCs) are shown in figure 3(b) and underscore the distinct effect caused by modulation of the spectral phase. For example, the SS peak maximum in the red curve (+441 fs$^2$ GVD) is visibly displaced by 55 meV and broadened by 56 meV, or 25%, when compared to the data recorded at a vanishing GVD (black curve).

3. Model

3.1. Laser field

The time-integrated 2PPE intensity in a narrow $k$-range around $k_{\parallel} = 0$ Å$^{-1}$ is proportional to the fourth power of the temporal electrical field, in analogy to a SH-like signal [36, 37]. In order to theoretically examine the consequences of a given spectral phase of a femtosecond laser pulse on the static 2PPE spectra, we calculate the spectral distribution of such a SH-like signal, which is generated by two photons from a phase-modulated 399 nm laser field.

The starting point for the calculations is the Gaussian spectral field distribution $E(\omega)$ as determined by the pulse duration $\tau_{TL}$ of a transform-limited laser pulse [38], that is modulated by a frequency dependent phase $\psi(\omega)$:

$$E(\omega) = \sqrt{\frac{\pi}{8\ln 2}} \tau_{TL} \exp \left[ -\left( \frac{\tau_{TL}^2}{8\ln 2} \right) (\omega - \omega_0)^2 - i\psi(\omega) \right].$$

(1)

$\psi(\omega)$ is modelled as an expansion about the carrier frequency $\omega_0$ [39]. In these calculations, only the GVD and TOD terms of this expansion are taken into account so that $\psi(\omega)$ is given by:

$$\psi(\omega) = \frac{1}{2} \text{GVD} (\omega - \omega_0)^2 + \frac{1}{6} \text{TOD} (\omega - \omega_0)^3.$$  

(2)

The numerically calculated inverse Fourier transform of $E(\omega)$ gives the complex temporal field $E(t)$ of the chirped pulse in the time domain. This expression is squared to yield the effective SH-like field responsible for the non-resonant two-photon excitation process [36], $E_{2n}(t) \propto (E(t))^2$. A Fourier transformation back to the frequency domain yields $E_{2n}(\omega)$, which is the spectral field distribution of the generated SH field, and is centred around 6.2 eV. For a quantitative comparison with the spectrally resolved 2PPE intensity distribution measured experimentally, we then calculate the spectral intensity $I_{2n}(\omega) \propto (E_{2n}(\omega))^2$.

3.2. GVD and TOD

To reconstruct the spectral response in the 2PPE experiment generated by the SH response of the laser field, a quantitative and complete knowledge of the experimentally applied GVD and TOD phase modulation is essential.
For the zero-position of the tuning prism, the GVD of the frequency dependent phase of the laser field vanishes at the sample position. As the first prism is translated further into or out of the laser beam, the total GVD of a phase modulated pulse is therefore determined only by the changing contribution from the prism material. The resulting net GVD can be calculated from the Sellmeier coefficients \( \text{Suprasil}\) at 399 nm with appropriate attention to the detailed geometry of the beam path through the prism. For our setup and wavelength, we find a value of \( \pm 368 \text{fs}^2 \) for a change in the GVD caused by translation of the tuning prism by \( \Delta h = \pm 1 \text{mm} \). A positive translation value refers to an increase of the amount of material in the beam, see figure 2.

However, the Fork prism pair set-up does not compensate for the GVD and TOD contribution at the same time \([31]\). At vanishing GVD, the total TOD value of the laser pulse at the sample is composed of both positive contributions from the material dispersion of the optical components in the setup and also a much larger negative contribution determined by the separation of the two prisms \([39]\). Hereafter, this ‘background TOD’ at the zero-position of the tuning prism will be referred to as TOD\(_0\). The value of TOD\(_0\) can, in principle, be approximated for a given experimental setup, but we treat it instead as a fitting parameter in our model of the experimental 2PPE data to check for self-consistency. Analogous to the GVD case, the total TOD will vary with the movement of the prism. This change in total TOD is calculated to be \( \pm 114 \text{fs}^3 \) for \( \Delta h = \pm 1 \text{mm} \). At this point, we are now able to express the spectral phase modulation of the femtosecond pulses passing through the Fork prism setup as a function of the prism translation \( \Delta h \) as shown below:

\[
\psi_{399\text{nm}}(\Delta h) = \frac{1}{2} (\Delta h \cdot 368 \text{fs}^2 \text{mm}^{-1}) (\omega - \omega_0)^2 + \frac{1}{6} (\Delta h \cdot 114 \text{fs}^3 \text{mm}^{-1} + \text{TOD}_0) (\omega - \omega_0)^3.
\]  

(3)

### 3.3. Parameter definition

The phase modulation applied to the 399 nm laser field \( E(\omega) \) results in spectral modifications to both the calculated SH-like intensity, \( I_{2\omega}(\omega) \), and the 2PPE intensity distribution of the Shockley SS, \( I_{2\text{PPE}}(\omega) \), as mapped in the CP-2PPE experiment. For meaningful comparisons between 2PPE experiments and \( I_{2\omega}(\omega) \)-calculations, we must consider in detail the peak position of the intensity maximum of both the 2PPE signal and the SH-like signal, \( X_{\text{2PPE}} \) and \( X_{2\omega} \), the FWHM values of their respective intensity distributions, FWHM\(_{2\text{PPE}}\) and FWHM\(_{2\omega}\), and, finally, the spectral asymmetry of the intensity distributions, \( \alpha_{2\text{PPE}} \) and \( \alpha_{2\omega} \).

Figure 4 shows a measured 2PPE energy distribution curve at \( k_1 = 0 \text{Å}^{-1} \) from the Shockley SS as a function of the energy above \( E_F \) to illustrate the procedures used to extract the necessary parameters from both the experimental data and theory. The displayed data set was recorded for a laser pulse exhibiting a GVD value of \( +441 \text{fs}^2 \) and a TOD value of \( -7063 \text{fs}^3 \). An asymmetry in the peak shape is clearly visible and we later show that this asymmetry is due to the phase modulation of the laser pulse. The phase modulation can distort the experimental 2PPE spectra to such an extent that finding the position \( X_{C,2\text{PPE}} \) of the 2PPE peak maximum using a conventional peak fitting routine is no longer reliable. In fact, the mismatch arising from such a procedure can be up to 14 meV (given by the difference between the peak position from the Voigt fit and \( X_{C,2\text{PPE}} \)) as illustrated by the blue dashed line in figure 4, which shows an attempt to fit the peak using a Voigt profile. The point-by-point difference between this fit and the experimental data is displayed by the blue bars in the viewgraph. Therefore, to account for
**Figure 4.** CP-2PPE spectrum of the Shockley SS for a phase modulation of GVD = +441 fs\(^2\) and TOD = −7063 fs\(^3\). The asymmetry parameter \(\alpha_{2\text{PPE}}\) is defined in (4) as \(\alpha_{2\text{PPE}} = (\text{FWHM}^L_{2\text{PPE}} − \text{FWHM}^R_{2\text{PPE}}) / 2\), half the difference between the left- and right-hand part of the FWHM, divided at the peak position \(X_{C,2\text{PPE}}\). For this measurement, the total peak asymmetry is 16 meV. The blue dashed line shows a fit of a Voigt profile to the experimental data. Fit and data are skew because of asymmetry in the peak introduced by the phase modulated pulse. This is emphasized by the column inset below the spectrum: the blue and red columns show the difference of the data to the blue (Voigt fit) and the red (smoothed data used to determine \(X_{C,2\text{PPE}}\) from the derivative) curves, respectively.

To quantify the asymmetry more accurately, we chose the approach described next to determine \(X_{C,2\text{PPE}}\). First, the noise in the experimental data is stripped away by a Fourier low-pass filter (see the solid red line in figure 4). Next, the numerical derivative of the smoothed trace is calculated and \(X_{C,2\text{PPE}}\) is then determined by the position at which the derivative crosses zero. For the calculated SH intensity distribution \(I_{2\omega}(\omega)\), the noise filter is not necessary, however \(X_{C,2\omega}\) is still determined from the corresponding derivative in a similar manner.

Both the experimental and theoretical FWHM values are obtained directly from the (smoothed) intensity distributions. Then, the contributions to the spectral width in the experimental data caused by the detector resolution (\(\Delta E = 20\) meV) and the intrinsic linewidth of the Shockley SS at room temperature (\(\Delta E = 65\) meV [40]) are subtracted quadratically.

Finally, to quantify the asymmetry of the traces, we define the asymmetry parameter \(\alpha_i\) as follows:

\[
\alpha_i = \frac{(\text{FWHM}^L_i - \text{FWHM}^R_i)}{2}, \quad i = 2\text{PPE}, \quad 2\omega, \quad (4)
\]

where FWHM\(^L\)\(_{2\text{PPE}}\) and FWHM\(^R\)\(_{2\text{PPE}}\) are the widths at half maximum of the left and the right sides, respectively, of the intensity distribution as separated by the position \(X_{C,i}\) of the intensity maxima, as shown for the 2PPE signal in figure 4. With definition (4), the asymmetry parameter is a measure for the displacement of \(X_{C,i}\) with respect to the FWHM centre.
However, a quantitative comparison between experiment and theory is only meaningful when comparing the relative changes due to the applied spectral phase. Therefore, we define \( \Delta X_{C,i} \) as the relative change in the peak position with respect to the peak position at vanishing GVD and the residual background TOD \(_0\):

\[
\Delta X_{C,i}(\text{GVD, TOD}) = X_{C,i}(\text{GVD, TOD}) - X_{C,i}(\text{GVD} = 0 \text{ fs}^2, \text{TOD} = \text{TOD}_0),
\]

\( i = \text{2PPE, 2ω} \). (5)

Calculations show that the asymptotic FWHM value reached at very large GVD values is identical to the FWHM of excitations with transform-limited pulses, i.e. with GVD = 0 fs\(^2\) and TOD = 0 fs\(^3\). Therefore, we can determine \( \Delta \text{FWHM}_i \) by subtraction of the asymptotic FWHM value for very large GVD values as shown below:

\[
\Delta \text{FWHM}_i(\text{GVD, TOD}) = \text{FWHM}_i(\text{GVD, TOD}) - \text{FWHM}_i(\text{GVD} \to \infty, \text{TOD} \sim \text{TOD}_0),
\]

\( i = \text{2PPE, 2ω} \). (6)

Definition (6) enables us to directly illustrate the impact of the ‘background LOD\(_0\)’ on the FWHM value for both experimental and theoretical data. The three parameters of interest, \( \Delta X_{C,i} \), \( \Delta \text{FWHM}_i \) and \( \alpha_i \) are evaluated in both the model and experiments as a function of the prism translation \( \Delta h \), i.e. as a function of the spectral phase modulation. Therefore, in the subsequent discussion, the results will be displayed as a function of the applied GVD and the applied TOD. To fit the calculated \( \Delta X_{C,2Ω}(\text{GVD, TOD}) \) traces to the experimental data, the TOD\(_0\) value and the pulse duration \( τ_{\text{TL}} \) are kept as free parameters. When these \( τ_{\text{TL}} \) and TOD\(_0\) values are known, the \( \Delta \text{FWHM}_{2Ω}(\text{GVD, TOD}) \) and \( \Delta \alpha_{2Ω}(\text{GVD, TOD}) \) curves are then calculated and directly compared with the experimental data without any scaling.

As a check on self-consistency, the optimum fit parameter combination (\( τ_{\text{TL}} \) and TOD\(_0\)) is compared with both autocorrelation measurements and an estimate of the amount of TOD picked up by the optical setup [38, 39, 40].

4. Results and discussion

4.1. Peak energy and FWHM

The clearly visible changes in the position of the peak maximum and FWHM as well as the appearance of asymmetry in the Shockley SS peak in the 2PPE energy distribution curve (EDC) caused by the application of GVD and TOD to the laser pulse have already been illustrated in figure 3. In the following discussion, the sensitivity of the 2PPE SS signal to the spectral phase will be quantitatively compared with the calculations from the theoretical model.

Figure 5 shows experimental \( \Delta X_{C,2\text{PPE}}(\text{GVD, TOD}) \) traces (black diamonds) and experimental \( \Delta \text{FWHM}_{2\text{PPE}}(\text{GVD, TOD}) \) traces (blue circles) together with the results from our calculations (solid lines) for 11.9 nm data (figure 5(a)) and 8.7 nm data (figure 5(b)). The data in figure 5 shows that spectral phase modulation results in changes that are clear and complex. For example, in the 11.9 nm data, the variation in the SS peak position follows an almost anti-symmetric dependence with respect to the zero-position of the tuning prism and also exhibits a maximum lift as large as 110 meV. The \( \Delta \text{FWHM} \) trace shows highly symmetric behaviour, whereas the minimum linewidth is measured only at vanishing GVD. For the 11.9 nm data, a maximum lift in the FWHM of 88 meV is observed. Overall, the effects of the broad 11.9 nm bandwidth on \( \Delta X_C \) and \( \Delta \text{FWHM} \) are enhanced by a factor of about 3 in comparison to the 8.7 nm data.
Figure 5. Experimental SS peak position values $\Delta X_{C,2PPE}$ (solid diamonds) and peak FWHM values $\Delta FWHM_{2PPE}$ (open circles) as a function of the GVD (bottom axis) and TOD (top axis) in comparison to the corresponding calculated traces (black and blue solid lines, respectively). (a) 11.9 nm data: the best agreement between experiment and theory is found for $\tau_{TL} = 19.7$ fs and TOD$_0 = -7200$ fs$^3$; the corresponding 8.7 nm calculations from graph 5 (b) are displayed as grey dashed lines for comparison. (b) 8.7 nm data: $\tau_{TL} = 26.9$ fs TOD$_0 = -8000$ fs$^3$ (solid lines). Peak position and FWHM change to a much smaller extent than for the 11.9 nm data. For comparison, $\Delta X_{C,2\omega}$ and $\Delta FWHM_{2\omega}$ data calculated for vanishing total TOD (TOD = TOD$_0 = 0$ fs$^3$) are also shown as dashed lines. Any deviations are completely absent in this case. For GVD = 0 fs$^2$ there are also no changes in $\Delta X_{C,2\omega}$ (not shown and identical to ‘no TOD’), however the $\Delta FWHM_{2\omega}$ value is clearly affected as shown by the dash-dotted line at the bottom of the graph (reference to the upper, TOD x-axis, only).
Figure 6. Change of SS peak position ($\Delta X_C$, black dashed curve) and FWHM ($\Delta$FWHM, blue curve), calculated with a resonant, long-lived intermediate state (as proposed in [27]) by OBE. The graph shows calculations by means of OBE that use the pulse parameters and model from [27] (pulse duration of $\tau_{TL} = 15$ fs, no TOD and optical relaxation time $\tau_0 = 10$ fs).

The calculated $\Delta X_{C,2PPE}$ trace displays the resulting fit to the experimental $\Delta X_{C,2PPE}$ data where the transform-limited pulse duration $\tau_{TL}$ and the TOD background $TOD_0$ are used as fitting parameters. With this method, it is possible to reproduce the experimental trace almost exactly. For the 11.9 nm data, a parameter combination of $\tau_{TL} = 19.7$ fs and $TOD_0 = -7200$ fs$^3$ yields the best agreement with experiment, whereas the optimum fitting result for the 8.7 nm data is achieved with $\tau_{TL} = 26.9$ fs and $TOD_0 = -8000$ fs$^3$. Both parameter combinations are consistent with separate time-resolved 2PPE (TR-2PPE) autocorrelation measurements and also with an estimate of $TOD_0$ [38, 39] from the optical setup used in these experiments. Furthermore, both parameter-sets are also consistent with experimental $\Delta$FWHM$_{2PPE}$ traces, which are clearly almost exactly modelled, too.

Previously, Petek et al. also observed this energy shift in the 2PPE signal from the Cu(111) Shockley SS peak as a function of the GVD chirp parameter [27]. However, in their work, the changes of the SS peak energy were attributed to the involvement of real substrate states at the energy level of the intermediate state in an indirect, intraband absorption process. Using a quantitative model based on the optical Bloch equations (OBE), the standard model to describe 2PPE processes involving a discrete energy spectrum at a surface [13], the authors did succeed to reproduce the peak shift behaviour in their calculated 2PPE spectra when they assumed an optical relaxation time of the involved substrate states of $\tau_0 = 10$ fs. However, the changes in the FWHM and the contribution of the TOD from the laser pulse were not considered.

In figure 6, we present the FWHM trace (and also the (quantitative) peak shift trace) corresponding to the simulated spectra from [27] as determined from equivalent simulations based on the OBE [39] and performed within this work. The calculations take into account
Figure 7. Change of SS peak position (left axis) and FWHM (right axis), calculated with an off-resonant (black and blue) and a resonant (grey) excitation scheme by OBE. All calculations are based on the 11.9 nm pulses ($\tau_{TL} = 19.7 \text{ fs}$, $\text{TOD}_0 = -7200 \text{ fs}^3$) and take the TOD into account. For comparison, the calculated curves from the SH-like model are shown as blue and black solid curves. A resonant, long-lived intermediate state (grey broken curves) leads to a significantly modified peak position curve and FWHM curve, whereas the SH-like model and the OBE with an off-resonant excitation scheme give the same results. The 2PPE peak asymmetry is correctly calculated by the OBE (non-resonant) as well (not shown).

the same model (optical relaxation time $\tau_0 = 10 \text{ fs}$) and the same pulse parameters (pulse duration $\tau_{TL} = 15 \text{ fs}$, TOD not considered) that also have been used in [27]. One finds that the slope of this FWHM trace evolves contrary to the slope observed in the experiment. The calculations in figure 6 as well as in [27] show a maximum in the FWHM at $\text{GVD} = 0 \text{ fs}^2$, whereas the experiments show a distinct minimum. This statement is obvious if compared to our experimental data, note, however, that it particularly holds also in direct comparison with the FWHM evolution in the experimental 2PPE spectra shown in [27].

In contrast, the model presented here does not rely on coupling to a resonant intermediate state exhibiting a finite lifetime and the data therefore require a different interpretation. In fact, our SH-like model assumes a non-resonant and, therefore, instantaneous coupling between initial and final states. Our model is able to reproduce both the $\Delta X_C$ trace as well as the $\Delta$FWHM trace in a quantitatively very satisfactory and self-consistent manner.

The validity of the used SH-like model in describing the 2PPE excitation from the Shockley SS is supported by a comparison with simulations based on the more complex OBE equations as shown in figure 7 under consideration of the determined $\tau_{TL}$ and $\text{TOD}_0$ values and the full spectral phase modulation as given in (3) for the excitation pulses. The OBE are solved for a three level system following the approach introduced in [13] where the Shockley SS and a free electron vacuum state act as the initial and the final states of the 2PPE process. The intermediate state level is handled as a non-resonant coupling to the $(n = 1)$ image potential state (see New Journal of Physics 11 (2009) 013016 (http://www.njp.org/))
figure 1), exhibiting in our case a detuning energy of $-1.5$ eV. The results of both simulations with respect to peak shift, FWHM and asymmetry are nearly identical. Note that the close relation between SH process and 2PPE has been emphasized before for instance in [37]. Figure 7 shows also results of Bloch-simulations based on the model introduced by Petek et al [27] under consideration of the experimental parameters used in this work. In both calculations the effect of the TOD has been considered. In comparison to the experimental data the distinct peaking effects in the resonant peak shift trace (grey broken curve) at GVD = $+500$ fs$^2$ and GVD = $-500$ fs$^2$ are clearly blurred and the minimum in the resonant FWHM trace (grey dotted curve) at GVD = $0$ fs$^2$ is less pronounced. The involvement of resonant real intermediate states obviously fails to reproduce the experimental findings.

We performed additional calculations with the SH-like model to evaluate in greater detail which parameters determine the observed spectral changes for a given pulse duration. First, we varied only the GVD term while keeping both TOD and TOD$_0$ at zero. In this case, the laser pulses are transform-limited for GVD = $0$ fs$^2$. The (labelled) dashed black and blue lines included in figures 5(a) and (b) show the result of this simulation for $\Delta X_C$ and $\Delta$FWHM. Without TOD present, the GVD parameter does not affect at all the peak position or FWHM. Next, we varied only the TOD term in the vicinity of TOD$_0$, while maintaining the GVD at zero. A pure TOD variation did not displace the peak position (not shown, identical to the no TOD – $\Delta X_C$ curve), but solely affected the FWHM of the SH signal (dashed-dotted line in figure 5). Specifically, $\Delta$FWHM became negative, which indicates ‘peak narrowing’. The narrowing becomes stronger as the available laser bandwidth increases. Additionally, there was a slight variation of the FWHM with the TOD value. This result is consistent with spectral narrowing in a frequency doubling process due to the cubic spectral phase, as discussed by Lozovoy and Dantus [41].

Together, these reference calculations make it clear that the spectral 2PPE modifications arise from interplay between GVD and TOD in that peak displacement and FWHM variations are determined and scaled by both the GVD and the amount of background TOD$_0$ (and with this, the total TOD).

On the other hand, calculations for different pulse durations at a given background TOD$_0$ show that both the maximum amplitude of the observed peak shift and the amount of ‘peak narrowing’ drastically increase with the laser pulse bandwidth. The large difference between the 11.9 nm and the 8.7 nm data clearly support these findings.

Therefore, we conclude that the peculiar chirp dependence of the 2PPE signal from the Shockley SS can be fully explained with a properly modelled spectral phase modulation and a SH-like process. This process mirrors the instantaneous 2PPE from the SS via a virtual intermediate state. Note that next to our experimental data, we also succeeded in quantitatively reproducing the experimental data from [27] (peak-shift, change of FWHM and, furthermore, interferometric two-photon time-resolved photoemission data) in a very satisfactory manner. The involvement of a real intermediate state due to the coupling of the excitation to the substrate electronic structure, as proposed in [27], is, therefore, not necessary.

4.2. Peak asymmetry

While peak displacement and peak broadening in the 2PPE signal may complicate a comparison with reference data from other work, as long as the phase modulation is kept constant within an experiment, these parameters will not significantly interfere with the data analysis. However, peak asymmetry strongly affects the quality of information gathered from a 2PPE
spectrum. Previously, peak asymmetries in photoemission experiments have been attributed to either limitations in the experimental energy resolution, to surface steps or to poor surface quality [42, 43]. The spectral phase peculiarities of a femtosecond laser pulse have not yet been considered in this context. The asymmetry data $\alpha_{2\text{PPE}}(\text{GVD, TOD})$ and $\alpha_{2\omega}(\text{GVD, TOD})$ presented in figure 8 together with the $\Delta X_C$ traces show good agreement between the experimental results and the theoretical curves calculated using $\tau_{\text{TL}}$ and TOD$_0$ values from the $\Delta X_C$ fit. For GVD-only pulses, the calculation predicts symmetrical peaks for all values (dashed line in figure 8), as well as for TOD-only pulses (dash-dotted line). Again, including the interplay between the GVD and the TOD terms is required to account for the experimental observations while the value of TOD$_0$ is found to govern the extent of the peak distortion by asymmetry.

From this data analysis, it becomes clear that the change in peak position is not a simple ‘displacement’ of the SS peak, but the appearance of asymmetry means that additional distortion of the peak shape takes place. Although the amount of asymmetry for the 8.7 nm data is small and hard to detect (+3 to −8 meV or 2 to 4% of the total FWHM), these values are still measurable and agree with theory. Therefore, for even longer pulses or smaller TOD values, the asymmetry from phase modulated pulses will be negligible. On the other hand, the 11.9 nm data show enhanced asymmetry with values ranging between −15 and +16 meV, which corresponds to 7% of the FWHM. A 2PPE peak fit at the extreme values of $\alpha_{2\text{PPE}}$ yields a peak fit curve that is skew with respect to the experimental 2PPE intensity data, as illustrated in figure 4. Shorter pulses or an increase in the TOD$_0$ value increase the maximum asymmetry even more. These measurements emphasize the fact that the use of very broadband femtosecond laser pulses in photoemission experiments requires a careful pulse compression even for static measurements to avoid a potentially misleading peak distortion arising from phase modulation.

5. Summary

By using phase-modulated femtosecond laser pulses, we were able to deduce a consistent picture of the excitation pathway responsible for the 2PPE photoemission from the Cu(111) Shockley SS. Restricting the theoretical analysis solely to the optical parameters of the exciting laser field enabled us to completely reproduce and explain with high accuracy and consistency all peculiarities of the SS peak in a CP-2PPE study at different experimental conditions. In addition, our theoretical SH-like model satisfactorily and quantitatively reproduced the observation (previously reported in [27]) of a SS peak shift of up to 110 meV, variations in the SS FWHM up to 88 meV (corresponding to a 55% broadening with respect to the measurement at vanishing GVD) and SS asymmetry, which was induced by phase modulation of the incident laser pulses. All these reported effects are caused by the interplay between GVD and TOD of the 399 nm laser pulse spectral phase. Additional calculations based on the much more complex OBE in a non-resonant excitation scheme confirm our theoretical analysis. The presented results allow relevant insights into the involvement of the bulk electronic background on surface localized nonlinear optical absorption processes. Our findings are of particular relevance for TR-2PPE studies where the Cu(111) Shockley SS has emerged as a standard reference system for laser pulse width analysis. Specifically, theoretical modelling of the TR-2PPE that includes TOD contributions from the real light field may improve data analysis, as previously demonstrated by Merschdorf et al [44]. Our work further emphasizes the relevance of the TOD contribution to the spectral phase analysis for such experiments and models.

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Figure 8. Experimental peak asymmetry $\alpha_{2\text{PPE}}$ (open squares) values compared to their corresponding calculations (red line). (a) 11.9 nm data and (b) 8.7 nm data. For comparison, the peak position change $\Delta X_C$ (diamonds and black line) is displayed. The calculations have been performed using the same values of $\tau_{\text{TIL}}$ and TOD$_0$ as for the data displayed in figure 5. The asymmetry modulations are much smaller than the changes in the peak position (compare the different scales on the left and right sides of the graphs). Close to vanishing GVD or at very large values, the asymmetry reaches zero, i.e. the 2PPE peaks are symmetrical. Without TOD, the peak remains symmetric independent of the GVD value (dashed horizontal line in both graphs). The same holds for absent GVD, where the asymmetry is constantly zero independent of the TOD value (dash-dotted line, top x-axis).
In future experiments, we propose that spectroscopy with chirped, i.e. phase-modulated pulses, can be used as a complementary method to both conventional 2PPE spectroscopy and TR-2PPE spectroscopy if characterized properly. The spectral and temporal modulations of the femtosecond laser-pulse in a CP-2PPE experiment allows access to ultrafast dynamical processes in a static 2PPE measurement that is beyond a classical linewidth approach, as previously shown, for example, in the Cs/Cu(111)-system [45, 46]. Therefore, a basic understanding of the nature of the two photon absorption process at the surface, as investigated in this work, is of essential importance for reliable interpretation of this type of data.

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