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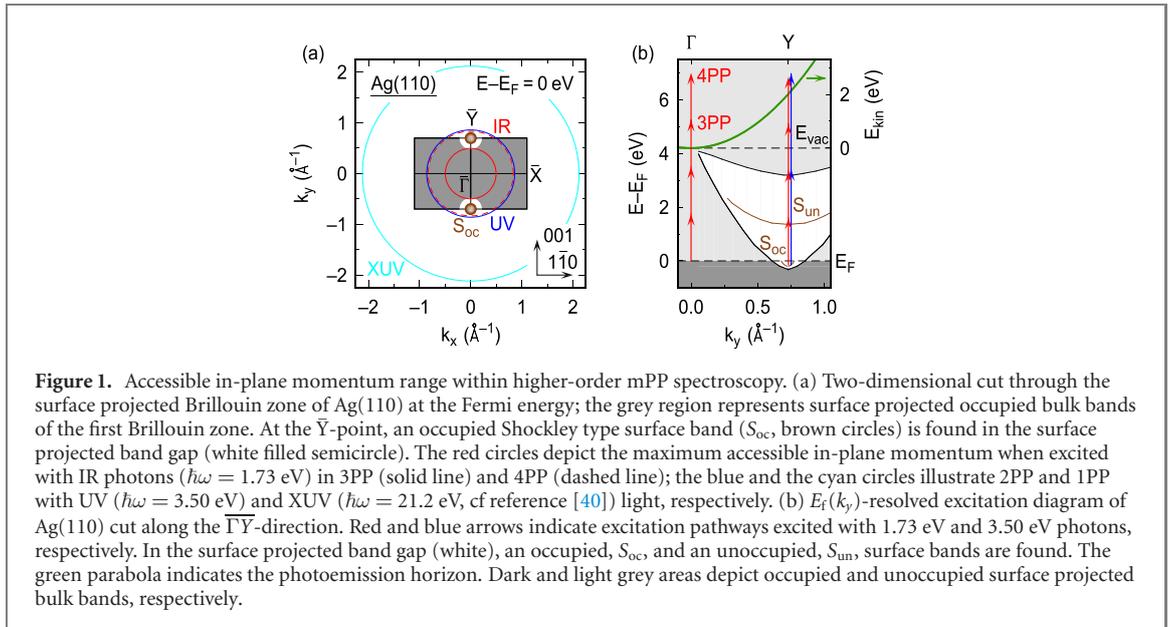
Andi Li¹, Namitha Ann James¹, Tianyi Wang¹, Zehua Wang¹, Hrvoje Petek¹ and Marcel Reutz²¹ Department of Physics and Astronomy and Pittsburgh Quantum Institute, University of Pittsburgh, Pittsburgh, United States of America² I. Physikalisches Institut, Georg-August-Universität Göttingen, Göttingen, GermanyE-mail: petek@pitt.edu and marcel.reutz@phys.uni-goettingen.de**Keywords:** coherent multi-photon photoemission, time- and angle-resolved photoemission, photoemission horizon**Abstract**

We report a novel approach for coherent multi-photon photoemission in the entire Brillouin zone with infrared light that is readily implemented in a laboratory setting. We excite a solid state material, Ag(110), with intense femtosecond laser pulses to excite higher-order multi-photon photoemission; angle-resolved electron spectroscopic acquisition records photoemission at large in-plane momenta involving optical transitions from the occupied to unoccupied bands of the sample that otherwise might remain hidden by the photoemission horizon. We propose this as a complementary ultrafast method to time- and angle-resolved two-color, e.g. infrared pump and extreme ultraviolet probe, photoemission spectroscopy, with the advantage of being able to measure and control the coherent electron dynamics.

1. Introduction

Time- and angle-resolved two-photon photoemission spectroscopy (TR-2PP) enables mapping the energy and momentum (k_x, k_y, k_z)-resolved electronic structure and dynamics of the occupied and unoccupied electronic bands of solids [1–3]. Using excitation frequencies from the infrared (IR) to the ultraviolet (UV) range, TR-2PP has been applied to a wide range of condensed matter systems ranging from pristine metals to complex materials and interfaces [4–17]. In TR-2PP spectroscopy, the photon energies $\hbar\omega$ of the pump and the probe laser pulses are chosen such that the pump excites the sample to a real or a virtual intermediate state and the probe induces a further upward transition from the excited system to induce photoemission. For photoemission to occur, the combined excitations must impart sufficient energy for the excited electrons to overcome the work function ϕ for $k_{x,y}$ near the surface and bulk Brillouin zone centre ($\bar{\Gamma}$ -point). To access the entire Brillouin zone, however, photoelectrons must be excited to sufficiently high energies to overcome the photoemission horizon. The photoemission horizon refers to the kinetic energy in the surface parallel motion, $E_{\text{kin}}^{x,y} = \hbar^2 k_{x,y}^2 / 2m_e$, which cannot do work against the work function because $k_{x,y}$ of electrons passing through a solid-vacuum interface is conserved [18, 19]. To induce two- or multi-photon photoemission (mPP), photoelectrons must absorb energy $m\hbar\omega \geq E_{\text{kin}}^{x,y} + E_B(k_{x,y}) + \phi$, where m is the photon order, m_e is electron mass, \hbar the reduced Planck's constant, and $E_B(k_{x,y})$ the in-plane momentum dependent initial state binding energy. Therefore, to map out $E_B(k_{x,y})$, i.e. the electronic structure and dynamics of occupied and unoccupied bands in full surface Brillouin zone, the experiment must overcome the photoemission horizon either by probing with higher $\hbar\omega$ or with higher-order mPP (cf figure 1).

While the unperturbed occupied electronic band structure spanning the full Brillouin zone is routinely measured with extreme ultraviolet (XUV) light available at synchrotron facilities or from gas discharge lamps, band mapping of the structure and dynamics of the unoccupied region requires wavelength tunability and ultrafast time resolution. Table-top high-harmonic generation (HHG) sources pumped by

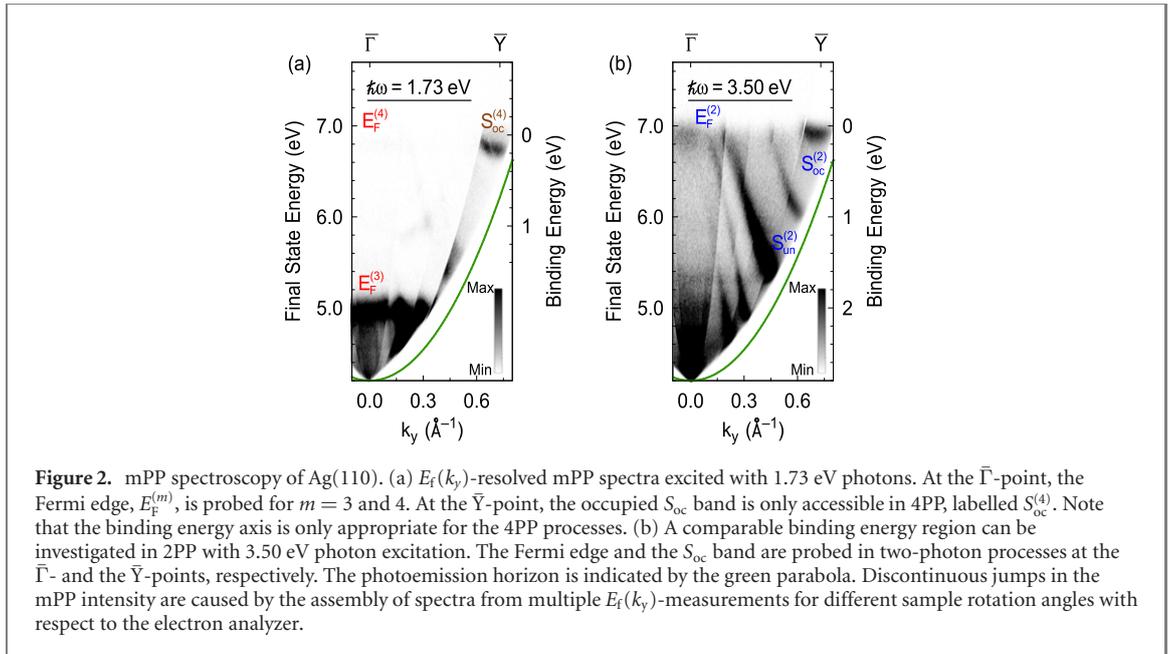


femtosecond laser amplifiers [20–24] and free-electron lasers [25, 26] can supply ultrafast XUV light pulses with $\hbar\omega > 20$ eV energy at high repetition rates. Such experimental setups have been applied to perform time- and angle-resolved photoelectron spectroscopy (TR-ARPES), where an intense infrared or optical pump-pulse excites the electronic system, and an XUV-probe pulse interrogates its impact on the electronic band structure of the sample. In this manner, excited-state band mapping becomes possible. In addition, the two-color electronic interaction has led to remarkable optical manipulation of exotic properties defined by reduced dimensionality, topological protection, and strong correlation [21, 23–25, 27–37].

In this article, we demonstrate a novel approach to create and characterize electronic excitations of solids in deep regions of the Brillouin zone that does not require XUV light, and gives access to the dynamical coherent manipulation of excitations at solid surfaces. Instead of generating high energy photons in a separate non-linear medium, we take advantage of the intrinsic non-linear response of the sample to realize a complementary (coherent) approach. We overcome the photoemission horizon by exciting higher-order mPP to achieve sufficiently high photoelectron energies to record photoelectron spectra at large in-plane momenta. More prosaically, we transfer the highly non-linear process otherwise used in the XUV light generation directly into the mPP process to potentially access additional information. We show proof of principle experiments by exciting the pristine Ag(110) surface with IR frequencies to detect the occupied Shockley surface band S_{oc} , centred at the \bar{Y} -point ($k_y \approx 0.7 \text{ \AA}^{-1}$) of the surface Brillouin zone, by 4PP via a one-photon resonance with an unoccupied Shockley surface band S_{un} .

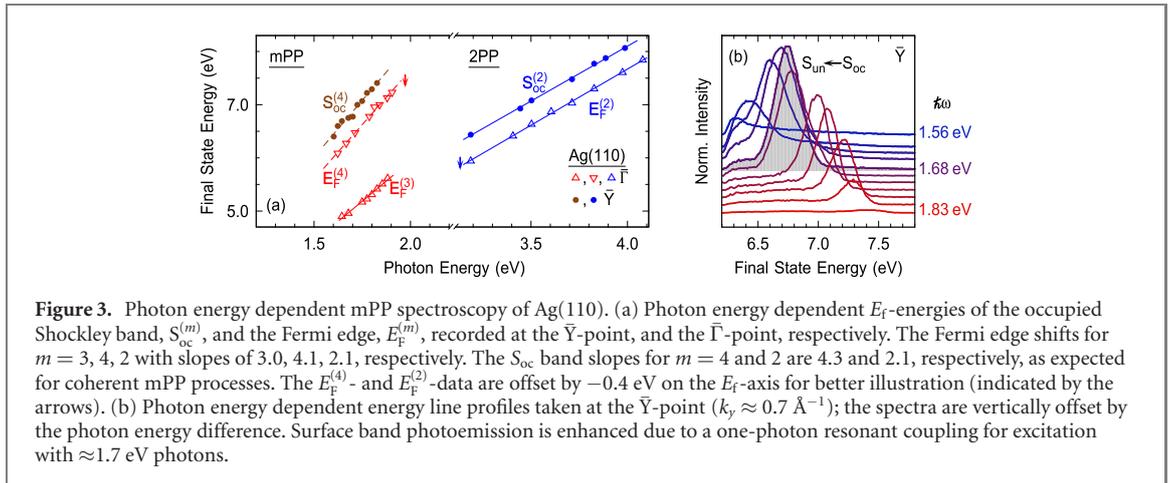
2. Results and discussion

We elaborate the proposed concept with the example of the pristine Ag(110) surface involving the following scenario (figure 1(a)): an energy slice at $E - E_F = 0$ eV shows a schematic 2D anisotropic (k_x, k_y)-resolved band structure of the first surface Brillouin zone of the (110) facet of silver [38, 39]. A Shockley-type occupied surface band S_{oc} exists in the surface projected bulk band gap with a minimum at the \bar{Y} -point (brown circles, $k_y \approx 0.7 \text{ \AA}^{-1}$). Its electronic and non-linear optical properties have been characterized by static ARPES using 21.2 eV light [40], scanning tunnelling spectroscopy [39, 41, 42], surface second harmonic spectroscopy (SSHG) [43], inverse photoemission [44, 45], and many-body theory [46]. In figure 1(a), the maximum accessible in-plane momentum that is expected for $\hbar\omega = 21.2$ eV is plotted as a cyan circle; because it encloses the \bar{Y} -point, S_{oc} is accessible in a conventional XUV-based ARPES experiment. In mPP with IR light, only electrons excited by intraband absorption involving three photon interactions and momentum scattering within the bulk sp-band are accessible at the $\bar{\Gamma}$ -point. The three-photon interaction (solid red line, $m = 3$), which is the lowest photon order m necessary to overcome the work function ϕ of Ag(110), defines the range of spectroscopic energy-momentum space that is accessible, yet the \bar{Y} -point and the S_{oc} band are out of reach. However, the S_{oc} band can be probed by increasing the non-linear order m of the photoemission experiment: In 4PP (dashed red line, $m = 4$), the S_{oc} band becomes experimentally accessible.



In the following, we demonstrate the proposed concept experimentally. We measure energy-, and angle-resolved mPP spectra of the Ag(110) surface at room temperature aligned so that its $\bar{\Gamma}\bar{Y}$ -direction is in the optical plane; details on the ultra-high vacuum system and the optical setup have been reported elsewhere [47–50]. In short, we generate tunable ~ 20 – 30 fs laser pulses with a noncollinear optical parametric amplifier (NOPA) [51] that is pumped at a repetition rate of 1 MHz by a Clark MXR fiber laser oscillator/amplifier system. The NOPA pulses are focussed to a fluence of 1 mJ cm^{-2} and an electric field strength of 10^9 V m^{-1} on the sample (estimated from the calculated beam diameter of $100 \mu\text{m}$). p-polarized light excites the Ag(110) sample at a 45° angle of incidence with respect to the detection axis of the hemispherical electron analyzer. Angle-resolved photoemission spectra are acquired with a 2D delay line detector. The angular acceptance angle of the analyzer is 26° . To record mPP spectra over a broader photoemission angle ($k_{||}$) range, the sample is rotated around the axis normal with respect to the optical plane; each of these energy- and angle-resolved measurements is integrated for approximately one minute. Note that to induce mPP from the \bar{Y} -point, the sample is rotated by approximately 55° , i.e. such that the laser incidence is nearly normal to the surface. Consequently, the optical field is effectively horizontally polarized such that it drives optical transitions in the $\bar{\Gamma}\bar{Y}$ -direction. This is an unusual circumstance for detecting an mPP signal, but is expected from the transition moment of the $S_{un} \leftarrow S_{oc}$ excitation, and polarization dependence of the SSHG signal that it mediates [43, 46].

Figure 2 shows final state energy- and momentum-resolved [$E_f(k_y)$] mPP data obtained from the Ag(110) surface; the corresponding energy diagram for excitation with $\hbar\omega = 1.73 \text{ eV}$ photons is shown in figure 1(b). In green, we plot the photoemission horizon, as obtained from $E_{kin}^{x,y}$; electrons excited to energies below this threshold *cannot* be detected unless they undergo momentum scattering within the sample to transfer kinetic energy from the surface parallel to normal motion and thereby alter their photoemission angle. At the $\bar{\Gamma}$ -point, we determine the work function of the Ag(110) surface to be $\phi \approx 4.2 \text{ eV}$, consistent with its reported values [52]. For excitation with 1.73 eV photons, three photons ($m = 3$) are sufficient to excite photoelectrons above the vacuum level at the $\bar{\Gamma}$ -point; electrons from the Fermi edge are projected to a final state corresponding to three-photon energy of $E_f \approx 5.2 \text{ eV}$. In the next higher order of photoemission, i.e. in 4PP, a replica of the Fermi edge is detected at $E_f \approx 6.9 \text{ eV}$, illustrating that the pump laser is sufficiently intense to excite higher-order multi-photon above threshold photoemission [49]. $\hbar\omega$ -dependent measurements confirm the assignment of these photoemission spectral features to three- and four-photon processes, respectively (figure 3(a)). By contrast, at the \bar{Y} -point ($k_y \approx 0.7 \text{ \AA}^{-1}$), three-photon absorption lifts electrons from the S_{oc} band to above ϕ , but still below the photoemission horizon, thus preventing their detection. Nevertheless, in 4PP, the S_{oc} band is raised above the photoemission horizon to $E_f \approx 6.8 \text{ eV}$ (figure 2(a)), enabling it to contribute to mPP spectra. The $\hbar\omega$ -dependent mPP spectra clearly identify that S_{oc} band contributes to mPP spectra through a four-photon process (figure 3(a)). We extract the binding energy of the S_{oc} band at the \bar{Y} -point to $E_B \approx 0.1 \text{ eV}$, which agrees with XUV-based ARPES experiments ($E_B^{lit} = 0.1 \text{ eV}$) [40]; minor deviations from the literature value can be attributed to the near-resonant excitation with spectrally broad femtosecond laser pulses. Additionally, we extract the



effective mass of the S_{oc} band from the data in figure 2(a) to values between $m_{eff} \approx 0.2-0.4$. While this value is consistent with the reported one $m_{eff}^{lit} = 0.26$ from ARPES experiments of Gerlach *et al* [40], we note that the S_{oc} band dispersion can be affected by a resonance condition in the mPP process, as we detail below. Thus, spectroscopic information on surface bands that are otherwise hidden below the photoemission horizon become accessible in higher-order mPP when exploiting the non-linear response of the sample.

We further identify details on four-photon excitation process by considering photon energy dependent energy line profiles taken at the \bar{Y} -point ($k_y \approx 0.7 \text{ \AA}^{-1}$) (figure 3(b)). Photoemission yield is clearly enhanced for photoexcitation with 1.7 eV photons, pointing towards a near-resonant one-photon coupling of the occupied, S_{oc} , and the unoccupied, S_{un} , surface bands, even though the S_{un} band does not appear as a distinct feature in the 4PP experiment in figure 2(a) (cf excitation diagram in figure 1(b)). Such enhancement of mPP via resonances of multiple surface bands is known for the (111)-facet noble metal surfaces [49]. Furthermore, this resonance between the Shockley surface bands is known from the enhancement of photon energy dependent SSHG on the Ag(110) surface [43].

The mPP data presented in figure 2(a) thus demonstrate that the non-linear energy conversion process typically applied in separate non-linear media to generate light of higher frequency can similarly be directly excited in a sample and detected through the mPP process. To illustrate the resemblance of both concepts, in the following, we first frequency double the infrared laser pulses in a BBO crystal outside the photoemission apparatus to obtain 3.50 eV photons. Accordingly, the maximum reachable in-plane momentum range widens; the \bar{Y} -point becomes accessible in a two-photon process (cf blue circle figure 1(a), $m = 2$). In 2PP (figure 2(b)), the S_{oc} band minimum is detected at $E_f \approx 6.9$ eV, corresponding to a binding energy of $E_B \approx 0.1$ eV with respect to E_F , which is in agreement with the 4PP measurement. Accordingly, the plot of E_f for S_{oc} vs $\hbar\omega$ has a slope of two (figure 3). We note, that the additional strongly dispersive bands in figure 2(b), which are less prominent though detected in 4PP in figure 2(a), are, to the best of our knowledge, not reported elsewhere in mPP or ARPES experiments. Even though the lifetimes of hot electrons for Ag(110) surface with UV excitation have been measured by TR-2PP [54], its spectra have not been reported. Multiple electronic bands have as well been observed in inverse photoemission spectroscopy, but not discussed in detail [45]. In addition, it is reported that the periodic surface corrugation replicates bands displaced by lattice wavevectors [39]. Tentatively, we assign these bands to contributions from many-particle effects [17], bulk transitions, as well as the unoccupied surface band S_{un} (labelled in figure 2(b)); we will report on these photoemission spectral features in a separate manuscript.

We further point out that the concept of the photoemission horizon and thus the necessity of sufficiently large kinetic energy photoelectrons to probe large in-plane momentum is a pure solid-state effect arising from space-periodic arrangement of the lattice atoms. This makes, for example, above-threshold multi-photon photoemission (ATP) [19, 48, 49, 53, 55, 56], a phenomenon accompanying mPP driven with IR frequencies, a two-dimensional problem. Conventionally, for mPP excited at the $\bar{\Gamma}$ -point, photoelectrons absorbing more photons than necessary to overcome the work function are treated as ATP. With increasing $k_{x,y}$, however, an electron populating a final state may not have sufficient energy in the surface direction to overcome the photoemission horizon. In our mPP data reported for Ag(110), this becomes obvious in figure 2(a), where 3PP at the $\bar{\Gamma}$ -point is sufficient to be detected and thus the replica structure in 4PP can be attributed to ATP; by contrast, at the \bar{Y} -point, 4PP is not an above threshold process but rather the lowest

order of photoemission. These considerations stand in contrast to ATP from nanostructured materials, where band momentum integrated processes obscure the origin of the photoelectrons and thus their in-plane momentum information. Instead, the local field enhancements determine the photoexcitation physics [57]. Similarly, the highly non-linear excitation of atoms and molecules, where the concept of above threshold ionization was initially developed [58], is not affected by the considerations discussed here, because $k_{x,y}$ is not a conserved quantity.

Finally, we comment on the complementary strength of two-color TR-ARPES, and one-color coherent mPP. We anticipate that for excited state band mapping, including the extraction of effective masses, as well as the measurement of the (incoherent) decay dynamics of hot charge carriers, TR-ARPES will provide more quantitative results than higher-order mPP. By contrast, coherent mPP can be applied in a phase-resolved pump-probe experiment, known as interferometrically time-resolved multi-photon photoemission (ITR-mPP) [2, 5, 6, 47, 48, 59–61]. ITR-mPP has been shown to be sensitive to optically induced coherent polarization fields oscillating at the driving laser frequency and its higher harmonics [2, 48]; dephasing times of coherences between coupled electronic bands have been extracted [62–64]. Beyond that, it has been shown that within highly non-linear light-matter coupling, the light field can be used to coherently manipulate the equilibrium band structure of the interrogated material via the AC Stark effect [50]. Such light-induced band structure engineering, so called Floquet engineering, is especially promising at long wavelengths and high electric field strengths as applied in our work [50, 68–70]. Moreover, it opens a new approach for performing measurements where the excitation field can both drive dipole transitions and intraband ballistic electron acceleration in solids [65–67]. Our work shows that such physics becomes accessible for electronic bands ranging deep into the surface Brillouin zone.

3. Conclusion

In conclusion, we report a coherent approach to perform photoemission spectroscopy, and measure the ultrafast electron dynamics of electronic bands extending deep into the Brillouin zone. Instead of providing large energy photons in the process of HHG, as typically done in optical-pump-XUV-probe TR-ARPES experiments, intense infrared light can be used to induce multi-photon processes leading to photoemission spectral features above the photoemission horizon. Proof of principle data obtained on the Ag(110) surface presented in this article thus provokes the application of mPP to novel materials whose physical and chemical properties are defined by their electronic band structure at the Brillouin zone edges, such as Dirac materials, or transition metal dichalcogenides. Thereby, higher-order mPP yield can be enhanced by resonant driving of selected dipole transitions [49], as well as by excitation at characteristic frequencies of the material's dielectric function, e.g. at the epsilon-near-zero condition, where the material's response is expected to be dominantly non-linear [17, 71]. We thus anticipate that time- and angle-resolved photoemission data from such materials will become increasingly accessible in typical laser-based photoemission laboratories without having to resort to XUV pulse generation. Furthermore, the presented methodology can be straightforwardly extended to novel photoelectron detection schemes, opening, for example, the door towards interferometrically time-resolved multi-photon momentum microscopy [72–76].

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