Time-resolved photoemission: the laserlab@uzh

Pavel Kliuiev, Adrian Schuler and Kay Waltar

Department of Physics, University of Zurich, 8057 Zurich, Switzerland

Universität Zürich[UZH]

1 High Harmonic Generation

1.1 Principle and method

The LASERLAB is equipped with a commercial femtosecond oscillator (Coherent MIRA seed, 67 MHz) and amplified with a high repetition rate regenerative pulse amplifier (RegA 9050, 30-300 kHz). The pulses (1.55 eV, 100 kHz) are then frequency doubled (3.1 eV) and focussed in an UHV chamber where Argon gas is excited and emits photons of 15.5 eV (5th harmonic). These light pulses are then focussed (B4C mirrors, optimized for 80 nm) on a target in the analysis chamber. By overlapping the XUV beam with the 800 nm fundamental which is left over after the frequency doubling spacially and temporally we are able to perform time-resolved angular photoemission spectroscopy (tr-ARPES) within the first Briouillin zone of our cristalline samples.
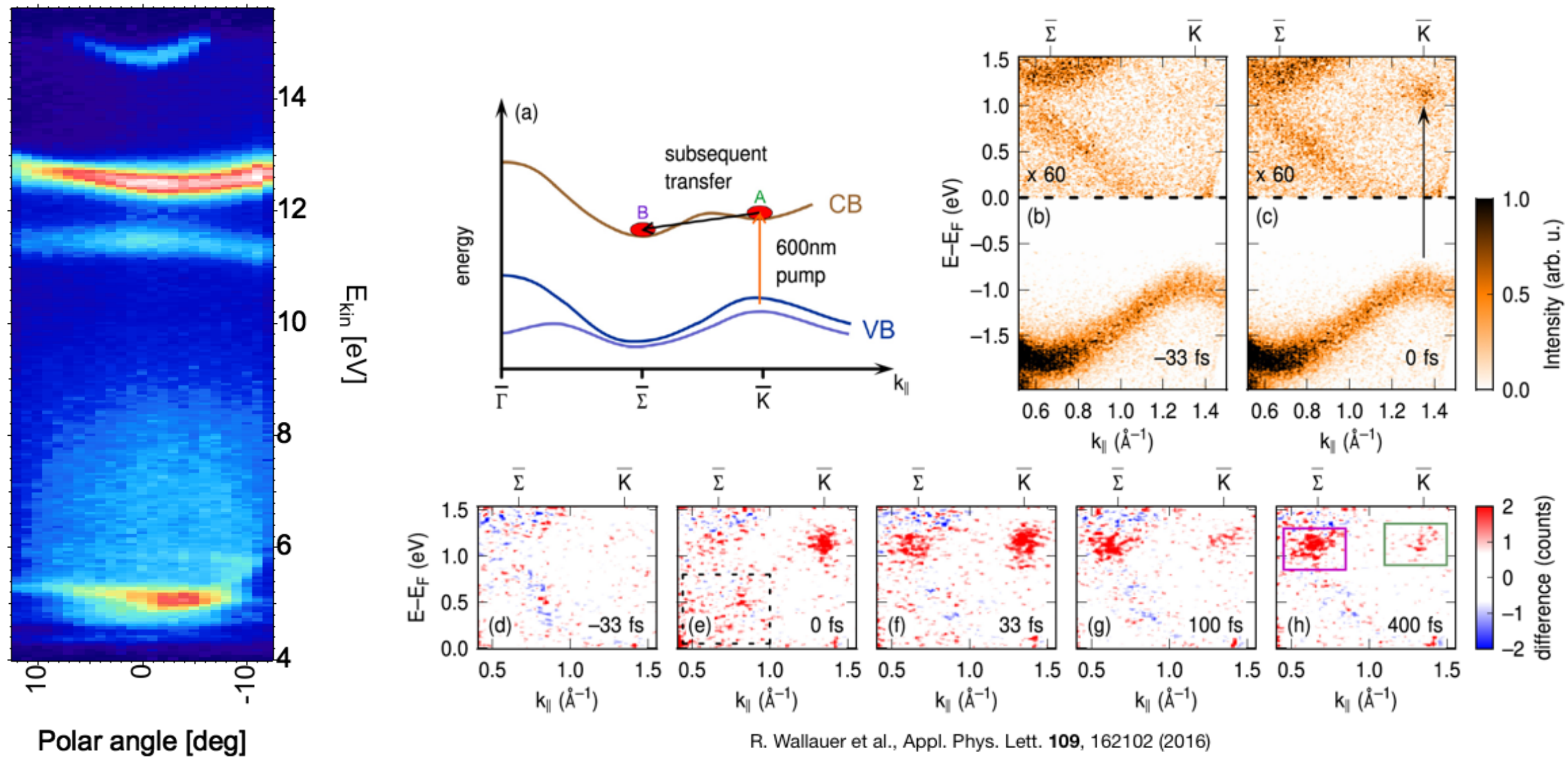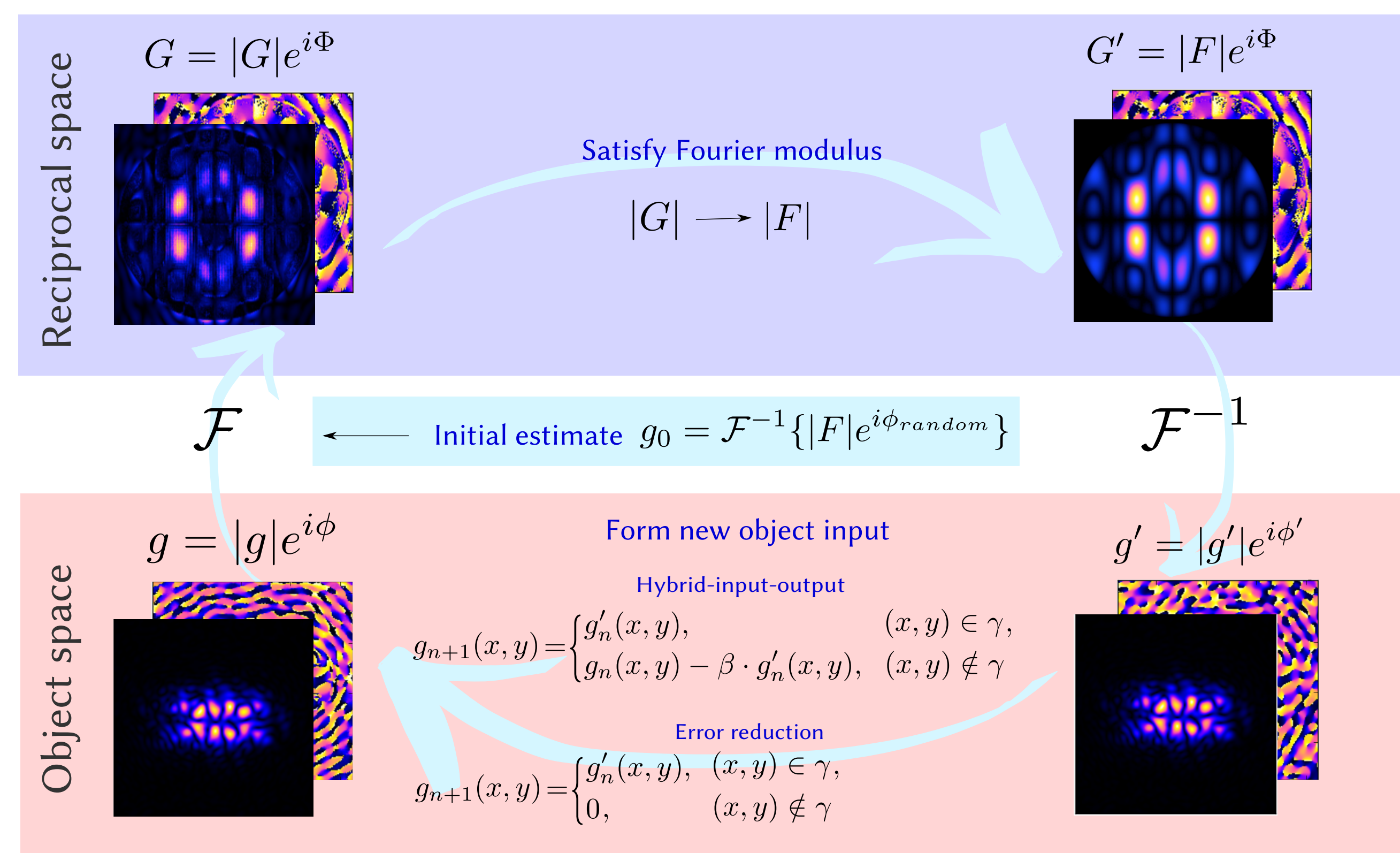

Left: First ARPES spectrum measured with only XUV (15.5 eV, 10^{11} photons/s, 200 meV resolution, 27 October 2017). Band structure of Cu(111). Right: tr-ARPES measurement from Marburg (Prof. U. Höfer). Unoccupied states of MoS_2 measured with a similar setup. Since the electrons are excited at the K point this requires high photon energies above 15 eV.

1.2 HHG setup

CATIA rendering of the HHG setup at the laserlab@uzh. Including the analysis chamber of the photoemission setup T-REx.

The fundamental for the HHG process (400 nm) is focussed into the HHG chamber where it passes the Argon gas and generates High Harmonics. A 200 nm thick Indum filter is mounted into a VAT valve which seperates the HHG chamber and the Mono chamber. The filter makes sure that we have a big pressure gradient between the 2 chambers and it blocks the fundamental. The divergent 5th harmonic is then refelcted at two mirrors in the Mono chamber. The first mirror collimates the beam and the second one focusses the light on to our target in the analysis chamber. The XUV passes a D-shaped mirror in the Cube chamber where the pump beam (800 nm) is reflected onto the sample.
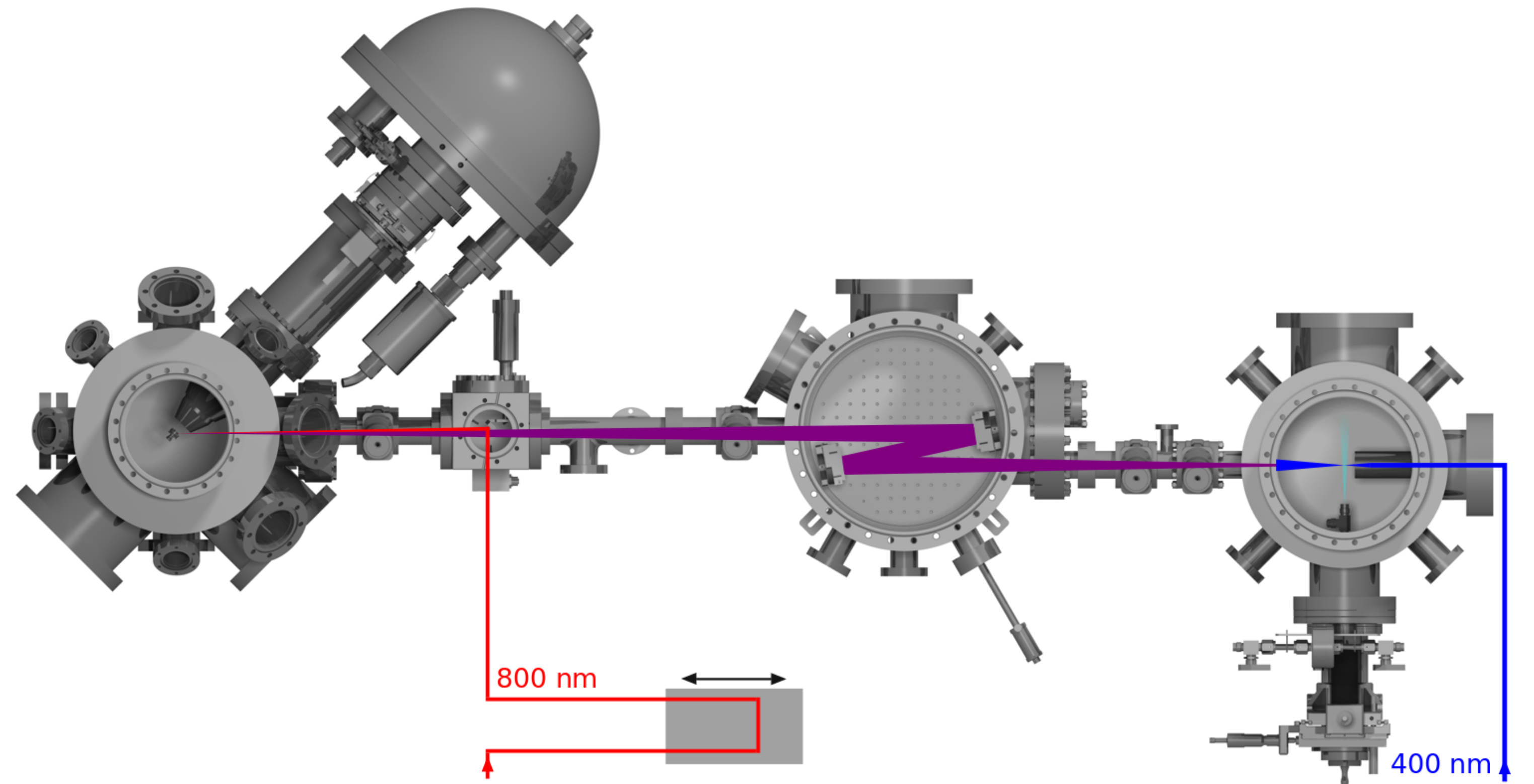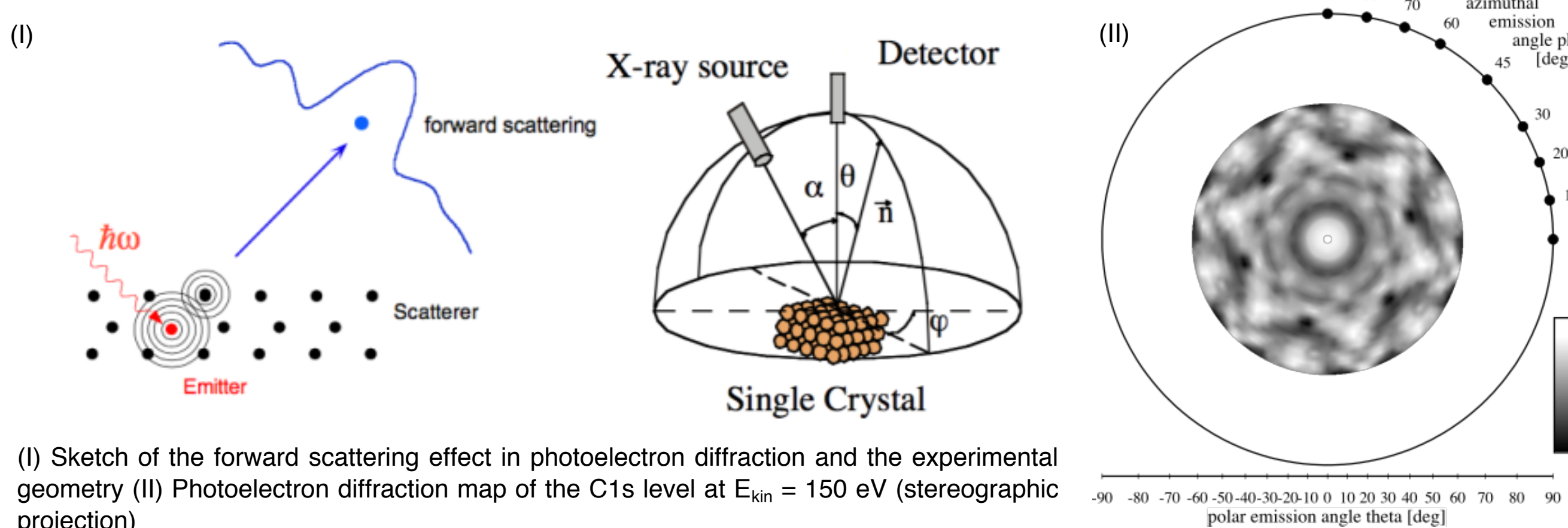
2 Orbital Tomography

2.1 Principle

For large planar molecules, consisting of light atoms (e.g. C, H, N), final state scattering can be neglected and the photoelectron final state can be well approximated by a plane wave [2.1], which makes photoelectron intensity distribution to be proportional to the squared modulus of the initial state wave function:

$$I(\theta, \phi; E_{kin}) \propto \sum_{f,i} \underbrace{|\langle exp(-j\mathbf{kr})| \mathbf{A} \cdot \mathbf{p} |\psi_i(\mathbf{r})\rangle|^2}_{\propto |\mathcal{F}\{\psi_i(\mathbf{r})\}|^2 = |\psi_i(\mathbf{k})|^2} \times \delta(E_f - E_i - \hbar\omega)$$

Reciprocal space

$G = |G|e^{i\Phi}$ $G' = |F|e^{i\Phi}$

Satisfy Fourier modulus

$|G| \longrightarrow |F|$

$\mathcal{F}$ Initial estimate $g_0 = \mathcal{F}^{-1}\{|F|e^{i\phi_{random}}\}$ $\mathcal{F}^{-1}$

Object space

$g = |g|e^{i\phi}$ $g' = |g'|e^{i\phi'}$

Form new object input

Hybrid-input-output

$g_{n+1}(x,y) = \begin{cases} g'_n(x,y), & (x,y) \in \gamma, \\ g_n(x,y) - \beta \cdot g'_n(x,y), & (x,y) \notin \gamma \end{cases}$

Error reduction

$g_{n+1}(x,y) = \begin{cases} g'_n(x,y), & (x,y) \in \gamma, \\ 0, & (x,y) \notin \gamma \end{cases}$

Unknown phase distribution in the detector plane prevents direct calculation of the initial state wave function via inverse Fourier transform. This issue is called the phase problem, which is well known from optics and is solved using iterative methods [2.2-2.4]. We employ a Shrinkwrap agorithm based on a combination of Hybrid-Input-Output and Error Reduction algorithms [2.5].

Measured ARPES map $\sqrt{I}$ Reconstructed wave function

$\mathcal{F}^{-1}\left\{|\psi_i(\mathbf{k})|e^{i\cdot arg\{\psi_i(\mathbf{k})\}}\right\}$

Iteratively retrieved phase

Fig.1.1 - Principle of iterative reconstruction of molecular wave functions

2.2 Reconstruction of Pentacene LUMO
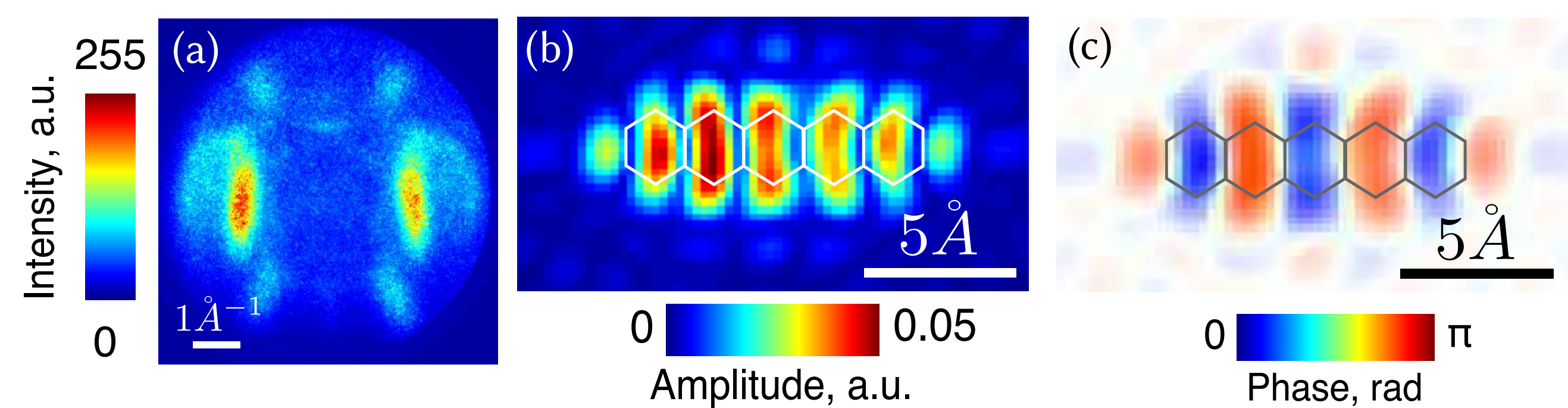
Fig. 1.2 - Reconstruction of pentacene LUMO from experimental ARPES data. (a) ARPES map recorded with photoemission electron microscopy (PEEM) from a sub-monolayer of pentacene on Ag(110) at 50 eV photon energy. (b) Reconstructed amplitude of pentacene LUMO. (c) Reconstructed phase of pentacene LUMO. Image transparency is weighed with the correspondent amplitude values for illustration purposes [5].
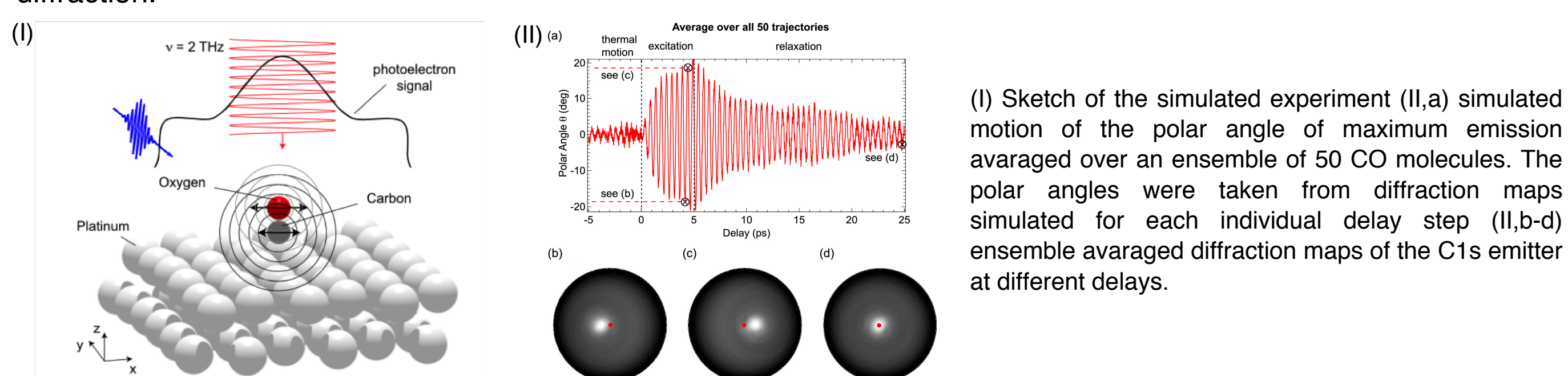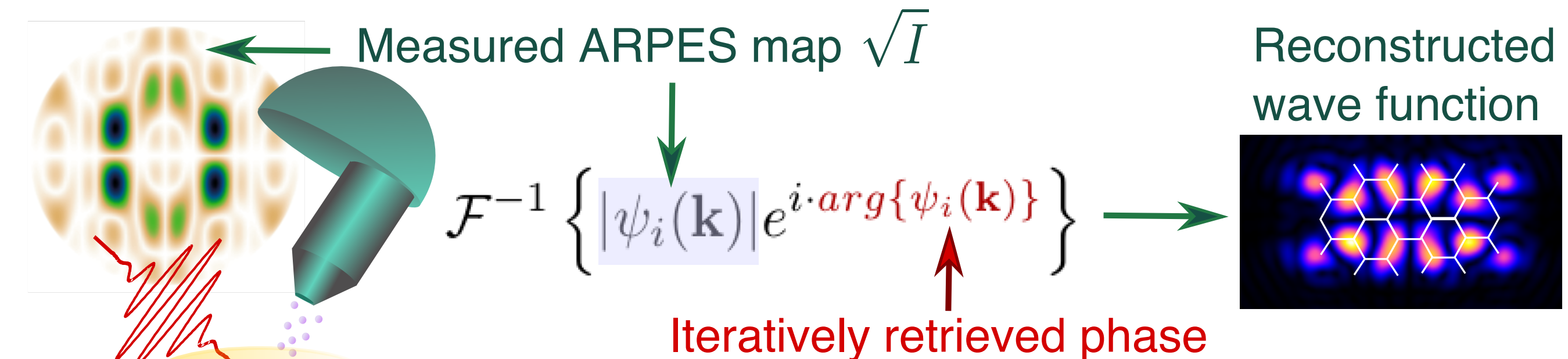
3 Photoelectron Diffraction

3.1 Principle and model system

Photoelectron diffraction is a suitable tool to investigate local surface structures. Owing to its chemical sensitivity the emitter atoms can be chosen. The main contrast mechanism is the forward scattering of the emitted photoelectron wave at neighbouring atoms. In combination with pulsed light sources it can be used to study structural dynamics of adsorbates.

(I) Sketch of the forward scattering effect in photoelectron diffraction and the experimental geometry (II) Photoelectron diffraction map of the C1s level at E_{kin} = 150 eV (stereographic projection)

The model system of carbon monoxide (CO) adsorbed on a Pt(111) surface provides a relatively simple system to study adsorbate structural dynamics. A few cycle THz-pulse can excite an ensemble of adsorbed CO molecules into a coherent frustrated translational motion [3.1]. This motion can in time be directly followed by photoelectron diffraction.

(I) Sketch of the simulated experiment (II,a) simulated motion of the polar angle of maximum emission avaraged over an ensemble of 50 CO molecules. The polar angles were taken from diffraction maps simulated for each individual delay step (II,b-d) ensemble avaraged diffraction maps of the C1s emitter at different delays.

### 3.2 Free electron laser THz-pump/XUV-probe experiment

At the FLASH free electron laser facility at DESY we performed a THz-pump/XUV-probe experiment in which a few cycle pulse of 1.8 - 2 THz was used to excite adsorbed CO molecules into a coherent motion. A subsequent XUV pulse was used to perform photoemission from COs valence orbitals.
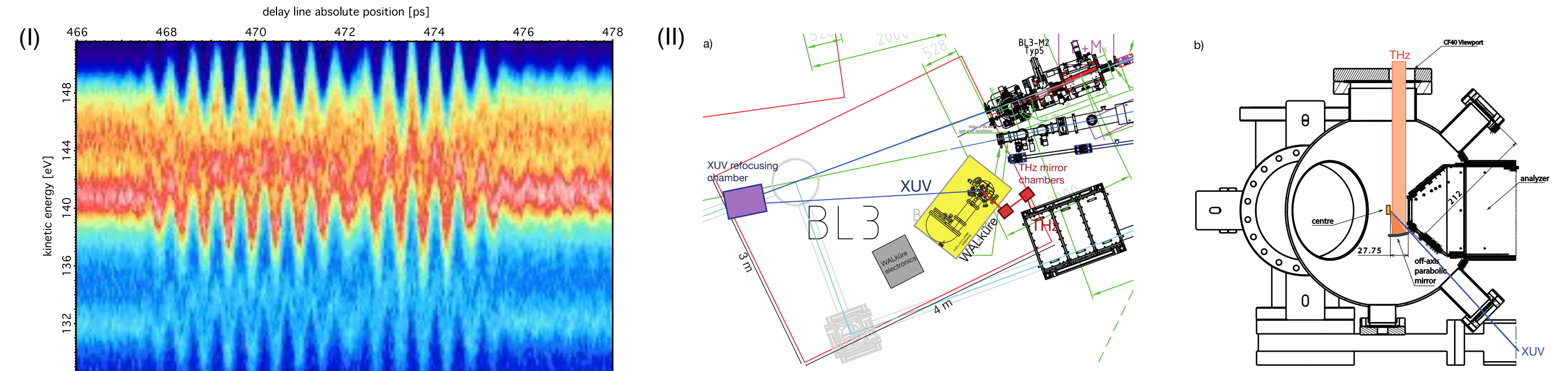
(I) Angle-integrated delay scan of the valence band region of a Pt(111) with a delay step size of 50 fs. E_{kin} = 140 eV, E_{pass} = 199 eV, f = 2 THz.
(II,a) overview of the experimental geometry at FLASH (II,b) experimental setup within the analysis chamber of our photoemission endstation.

3.3 Estimation of THz electric field strength

The amplitude of COs molecular tilt during the time-resolved photoelectron diffraction experiment is depending on the local strength and direction of the electric field at the substrates surface. These parameters can be obtained by analysis of the delay scan data.
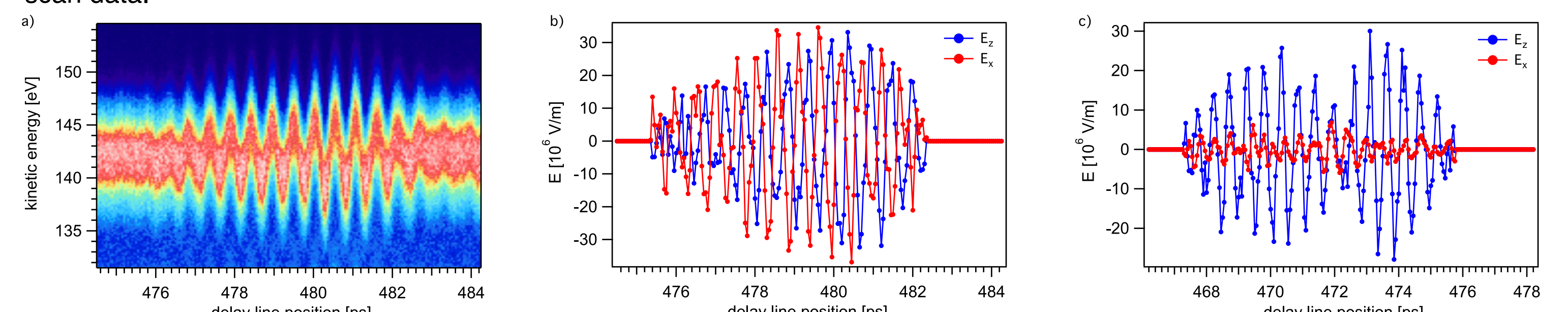
(a) Angle-integrated delay scan of the valence band region of a Pt(111) thin film sample with a delay step size of 50 fs. E_{kin} = 140 eV, E_{pass} = 199 eV, f = 2 THz. (b) Estimated strength of the electric field components parallel (E_z) and perpendicular (E_x) to the sample surface for the Pt(111) thin-film (c) Estimated strength of the electric field components for a Pt(111) bulk sample

References

[2.1] P. Puschnig et al. Science 326, 702 (2009); [2.2] J. Miao et al. Nature 400, 342, (1999); [2.3] J. Fienup. Opt. Lett. 3, 27 (1978); [2.4] S. Marchesini et al. PRB 68, 140101 (2003); [2.5] P. Kliuiev et al. New J. Phys. 18, 093041 (2016);
[3.1] M. Greif et al. Struct Dyn. 2,093102 (2015);

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