A Coherent White Paper

Time-Resolved Angle-Resolved Photoelectron Spectroscopy (TR-ARPES) using VUV Pulses

Scientists at Elettra-Sincrotrone, Trieste, Italy, use a novel scheme to generate VUV pulses at 10.8 eV (115 nm) from a Coherent Monaco amplifier to deliver a combination of high repetition rate (1-4 MHz) and small pulse-bandwidth that sets a new experimental standard in time-resolved ARPES measurements.

The TR-ARPES Method

Based on the photoelectric effect, photoelectron spectroscopy has long been used to analyze the electronic structure of samples ranging from small molecules to extended crystalline lattices. In its most basic form, the sample is irradiated with monoenergetic high energy (e.g., vacuum ultraviolet, VUV) photons causing the sample to emit electrons. These are then sorted according to their kinetic energy, usually by deflection in an electric field, and then quantitatively measured or counted in a detector. The kinetic energy of the photoelectrons is governed by the simple equation

$$E = h\upsilon - W - E_B$$

Where $h\upsilon$ is the photon energy, W is the work function of the sample, and E_B is the binding energy of the electrons. Since W is a constant and $h\upsilon$ is fixed and set by the photon source used, measuring the kinetic energy of the released electrons enables their binding energies to be directly determined. In molecules the photoelectron spectrum – the plot of electron intensity vs. energy – reveals the pattern of occupied molecular orbitals, and in semiconductors it shows details of the valence band structure.

Initially, photoelectron spectroscopy was performed using atomic lamps as the source of monoenergetic VUV photons but the advent of lasers greatly improved the analytical capability of this technique. Specifically, the ability to focus the laser source to a small spot enabled the angular trajectories of the emitted electrons to be analyzed relative to the sample, i.e., referenced to the lattice vectors in crystalline materials. This is usually performed by stepwise rotation of the sample stage with respect to the electron energy analyzer. Angle-Resolved Photoelectron Spectroscopy (ARPES) enables the detailed measurement of important information such as the shape of the Fermi surface, as a function of reciprocal cell vectors (k_x, k_y). Some researchers also incorporate a device called a Mott polarimeter that essentially measures the spin of the electrons.

ARPES can thus measure all the key scalar and vector properties of electrons in the band structure.

And by taking advantage of the short pulse width capability of lasers, scientists were able to further extend ARPES to obtain time-resolved data, i.e., TR-ARPES. Here a short pulse of photons (visible or near-IR) with an energy exceeding the sample bandgap excites electrons from the valence band into the conduction band and isfollowed by a probe pulse of VUV photons to cause photoelectric emission. Analysis of the energy and trajectories of the electrons therefore includes information about the conduction band. By varying the pump-probe delay, relaxation decay times and pathways of the conduction bands can be measured.

As a result, TR-ARPES has become established as a definitive research tool for studying new solid-state materials including cuprate superconductors, novel semiconductors, topological insulators, potential photovoltaic materials, and so forth.

Limitations of Existing Methods for VUV Pulses

Not surprisingly, the data quality and range is very dependent on the properties of the VUV pulses, particularly for TR-ARPES. The photon energy (i.e., wavelength) is arguably the most important parameter. Solid state materials scientists are typically interested in measuring electrons with momenta spanning the first Brillouin zone; in most quantum materials the edge of the Brillouin zone is at >1 Å-1.

For a sample rotation of say 45°, reaching electron momentum values >1 Å-1, requires a photon energy of 10 eV or more, i.e., a wavelength < 124 nm.

A small pulse bandwidth is also important to minimize the trade-off between energy and time resolution inherent in ultrafast laser pulses. Ideally TR-ARPES requires close to the transform limit with pulse widths < 1 ps which is fast enough to follow typical relaxation processes in quantum materials, while delivering energy resolution < 30 meV.

In addition, a high pulse repetition rate is desirable. A complete time-resolved and angle-resolved data encompasses myriad individual data points. To deliver this data set with acceptable signal to noise requires a high (MHz) pulse repetition rate. That's because the maximum pulse energy must be set quite low: below the threshold for creating space-charge problems, where the escaping electrons cause a repulsive field lowering the energy and momentum resolutions and thereby preventing accurate measurement.

Several methods for generating VUV pulses have been previously demonstrated for TR-ARPES but all have some type of limitation. For example, a synchrotron can deliver the short wavelength and small beam size, but the time resolution of tens of picoseconds is too slow for measuring electron dynamics. Alternatively, a free electron laser (FEL) can easily deliver the requisite short

wavelength and time resolution, but the very low repetition rate (< 1 kHz) makes it an impractical source for comprehensive TR-ARPES measurements.

Various laser-based tabletop systems based on non-linear effects in gases and crystals have therefore been used for TR-ARPES, with varying levels of success. The two common methods are harmonic generation in nonlinear crystals and high harmonic generation in jets of noble gases.

There are numerous optical crystals with non-centro symmetric properties and high non-linear coefficients, such as beta barium borate (BBO). These support efficient frequency conversion processes such as second harmonic generation (SHG) and sum-frequency generation (SFG) that can be combined serially to reach short wavelengths from near infrared laser input. However, their bandgap means that they absorb light in the deep ultraviolet and thus the practical photon energy limit that can be reached is about 7.5 eV. This is well short of the energy requirement for reaching the edge of the first Brillouin zone.

Tight focusing of pulses from a titanium:sapphire femtosecond amplifier into a jet of noble gas causes ionization followed by recombination. The recombination generates a cascade of high harmonics reaching far into the VUV. But this HHG process needs a high input pulse energy which limits the practical amplifier repetition rate to 250 kHz or less, limiting data throughput. Plus the entire process is highly sensitive to alignment and beam parameters.

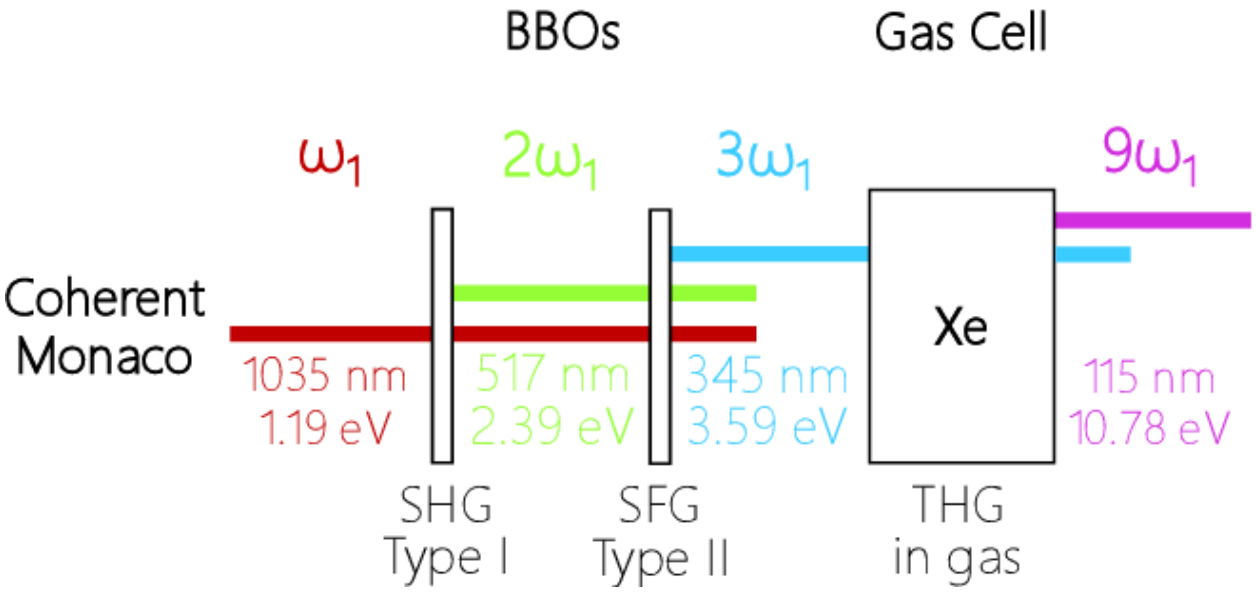

Figure 1. The 1035 nm output of a Monaco amplifier is efficiently upconverted to the 9th harmonic at 115 nm in a three-step process.

Frequency Upconversion with Monaco

Several groups have also investigated generating VUV by first creating ultraviolet pulses and then frequency tripling these pulses in a four-wave mixing process in xenon gas either in a cell or a hollow fiber. In a couple of instances, the VUV pulses have been used in equilibrium ARPES and TR-ARPES. A group led by Fulvio Parmigiani and Federico Cilento at Elettra-Sincrotrone, Trieste, Italy, have significantly extended this concept and combined it with a next generation ytterbium-based (Yb) ultrafast amplifier with a MHz repetition rate – the one-box Monaco from Coherent. This has allowed these researchers to set a new standard in TR-ARPES system performance, combining high photon energy, excellent energy resolution, and high throughput from a stable easy-to-use setup. Moreover, the high efficiency of their method means that they can use just part of the Monaco output to generate the VUV, leaving plenty of the near-IR available to use as a pump for pump-probe TR-ARPES, e.g., for interrogating conduction band details.

Their three-part process for generating VUV pulses is outlined in figure 1. The key final step of generating the VUV involves third harmonic generation (THG) in a cell filled with xenon. This is possible in wavelengths close to 115 nm, because in this wavelength window, xenon exhibits anomalous dispersion which enables phase matching of the 345 nm input and 115 nm THG output. The VUV is then separated from the 345 nm UV using a LiF wedge prism.

The 345 nm pulses are generated from the 1035 nm of the Coherent Monaco using two BBO crystals. The first is cut as a type-I crystal to enable efficient SHG doubling of the 1035 nm pulses to create 517 nm. The residual 1035 nm fundamental and the 517 nm are then mixed in a type-II BBO crystal generating 345 nm output in an efficient SFG process.

The overall conversion of the 1035 nm fundamental output to the 9^{th} harmonic at 115 nm is quite efficient: as high as 10^{-4}. As previously explained, this 10.78 photon energy is sufficient to span the first Brillouin zone in most materials of interest.

The way this VUV light is deployed in their TR-ARPES setup is outline schematically in figure 2. Several other aspects of this system merit further discussion. The Monaco pulse width is ~290 femtoseconds resulting in VUV pulses with a pulse width of about 300-400 fs. The delay between near-IR pump pulses and VUV probe pulses is controlled by a mechanical translation stage in the pump beam path. This time resolution is optimum for studying relaxation, recombination, and other dynamic processes in many quantum materials. The spectral bandwidth of the 115 nm light has been estimated to be of the order 10 meV. This is less than the TR-ARPES system ultimate energy resolution, which is limited by the hemispherical electron analyzer to about 26 meV.

At a base repetition rate of 1 MHz, the average power of the Monaco amplifier is 40 watts. The repetition rate can be lowered down to the single shot level, using a pulse-picker built into this Yb amplifier. Alternatively, the repetition rate can be increased up to 50 MHz, with a corresponding decrease in pulse energy.

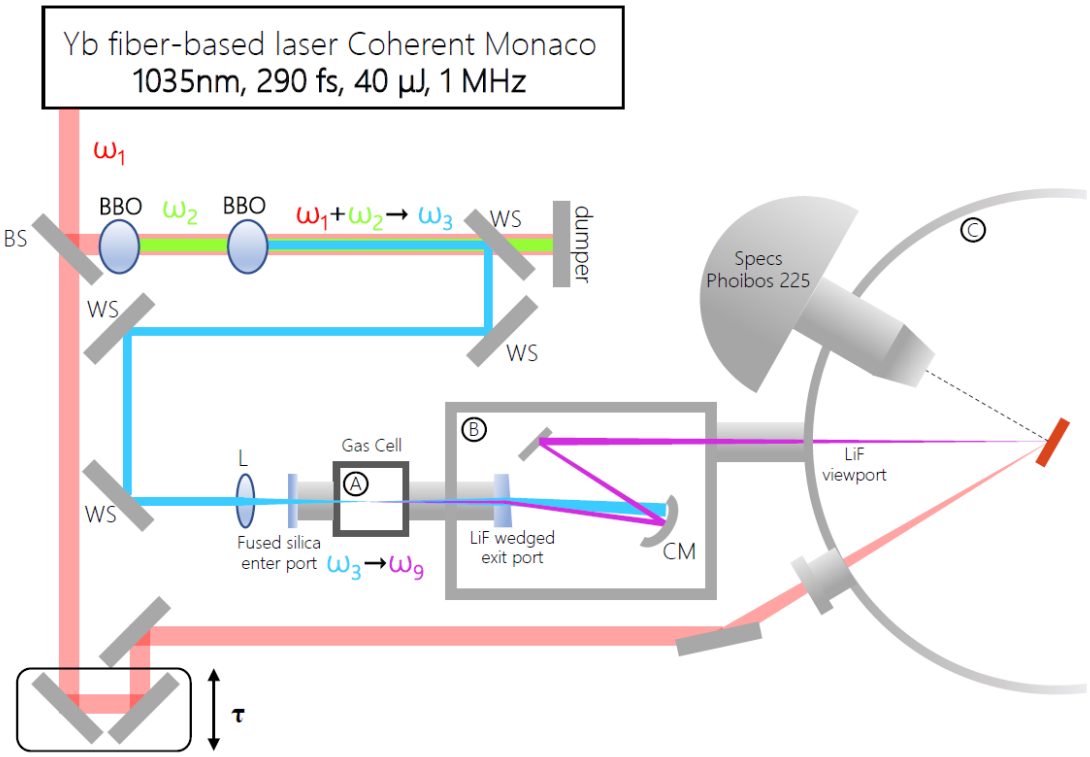

Figure 2. The main elements of the T-ReX TR-ARPES system at Elettra.

The combination of a high and flexible repetition rate, high conversion efficiency and high average power of the amplifier enables these researchers to optimize their TR-ARPES to maximize the signal to noise, while minimizing overall data acquisition times and limiting the VUV pulse energy below the onset of space-charge problems.

Professor Parmigiani explains the context of their system, "Our time-resolved VUV ARPES experimental setup ranks in first place in terms of throughput, photon energy, energy resolution, stability and reliability and in one of the first places in terms of time resolution." He notes that they have the option of manipulating the linear polarization of the VUV light with a λ/2 waveplate and the system's modest spatial resolution (focused VUV ~260 µm diameter) could be easily further improved if required, by optimization of the delivery optics.

Case Study Data on WTe_2 and Bi_2Se_3

The group have so far demonstrated these capabilities by performing detailed TR-ARPES case studies of two materials: a topological insulator, bismuth selenide (Bi_2Se_3), and the semimetal tungsten telluride (WTe_2).

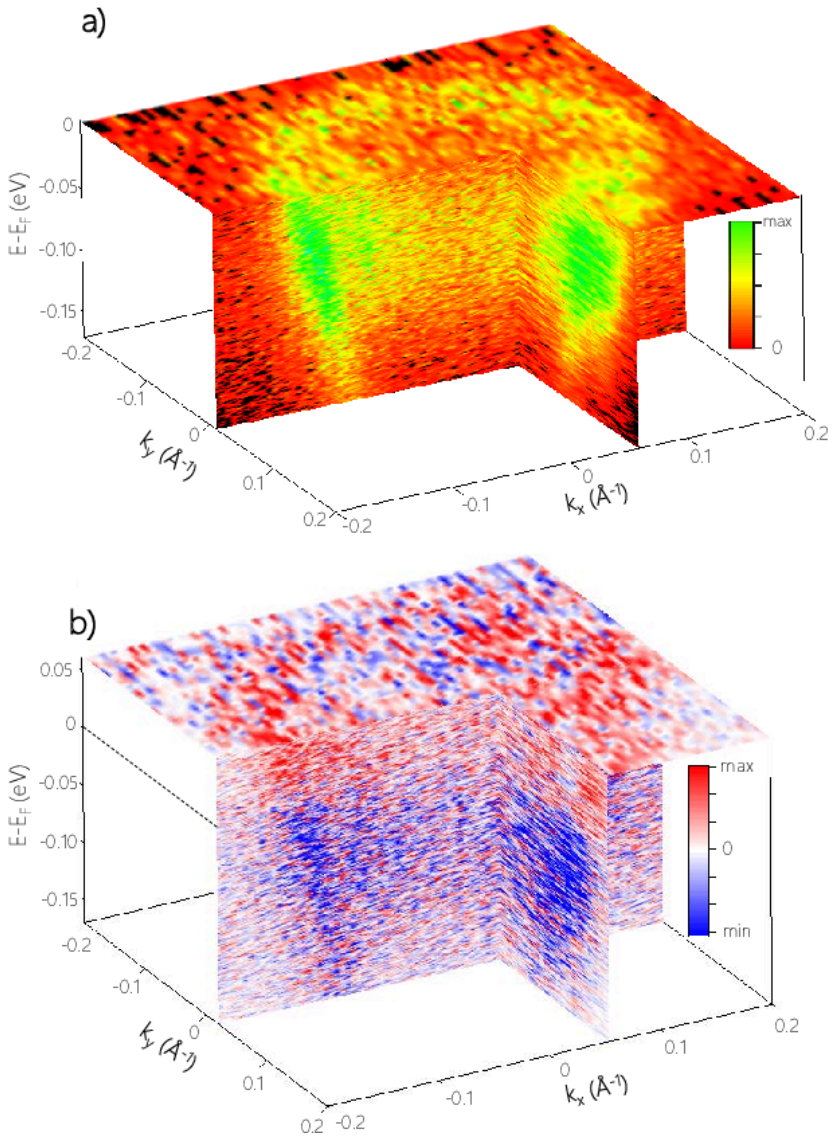

Figure 3. Some typical Bi_2Se_3 data. The top panel shows the equilibrium (steady state) photoemission intensity as a function of three-dimensions, E, k_x, k_y. The lower panel shows the differential map where the equilibrium data plot is subtracted from a pump-probe excited dataset with a delay of 1 ps time.

Thanks to their unusual surface energy states, topological insulators have been widely studied and proposed as candidates for spintronics and quantum computing based on spin coherence. Specifically, materials like Bi_2Se_3 are characterized by an energy gap between the valence and conduction bands in the bulk material but a gapless topological surface state (TSS) at their surface. Figure 3 shows some results from this study: equilibrium ARPES data at a pump-probe delay of 1 ps, where photoemission intensity (I) is dispersed relative to three parameters, E, k_x, k_y. Figure 4 shows some typical time-resolved (TR-ARPES) data. This series of images shows the observed time evolution of a two-dimensional (E, k_x) intensity map at several different pump-probe delay times. The corresponding map of the known (published) band structure is included in this figure, showing how closely their data matches the existing literature parameters.

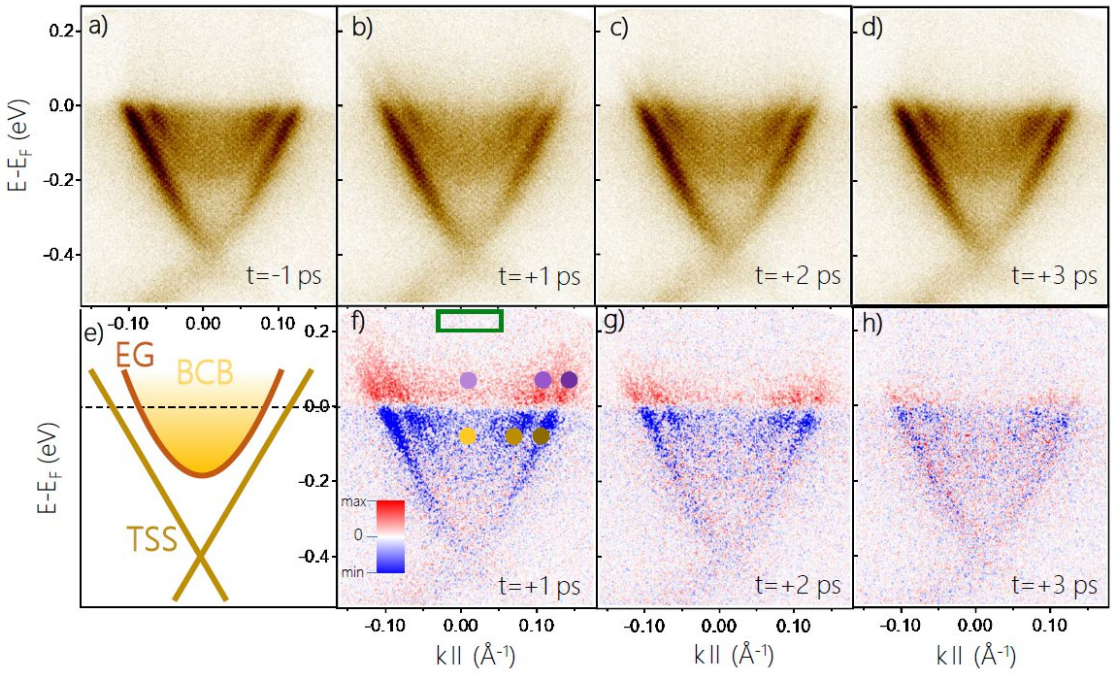

Figure 4. Dynamic Bi_2Se_3 data. The four upper panels show the time evolution of a two-dimensional (E, k_x) map at k_y = 0, for different pump-probe delay times. (e) shows the previously published spectral features. (f-h) show the differential maps where the t = -1 (i.e., equilibrium) plot is subtracted from the measured plots at the different delay times.

The Weyl type semimetal WTe_2 is of growing interest because of its non-saturating magnetoresistance and the discovery of pressure induced superconductivity. It has unusual tilted band details and the Elettra team have successfully used their TR-ARPES setup to visualize these details at equilibrium as well as for the excited band structure as detected at a 1 ps pump-probe delay. Figure 5 shows typical plots of I (vs. E, k_x) at k_y = 0. Parmigiani explains that, "These measurements prove that the photon energy of our experimental setup allows us to reach large momenta while maintaining a small tilt angle of the sample and with excellent signal to noise."

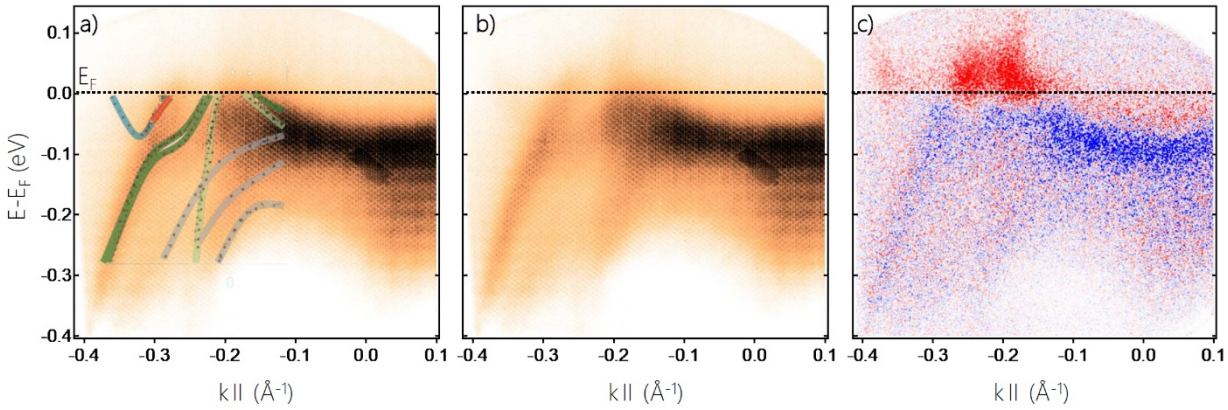

Figure 5. WTe_2 data. (a) equilibrium plot, (b) pump-probe delay of 1ps, (c) differential plot of b minus a. The overlay of lines indicate published data for electron pockets (blue) and hole pockets (green) showing the excellent detail and correspondence in this new data.

Summary

Parmigiani concludes that, "Thanks to new levels of ultrafast amplifier performance from the Coherent Monaco, we have been able to develop and demonstrate a new operating regime of VUV pulses for use in TR-ARPES. Together with the six degrees of freedom of the manipulator, these unique VUV pulse characteristics enable us to measure the out-of-equilibrium photoemission intensity I as a function of four parameters (E; kx; ky; t) over the complete first Brillouin zone of most materials."

Figures

All figures reproduced with permission of the authors of Simone Peli, Denny Puntel, Damir Kopic, Benjamin Sockol, Fulvio Parmigiani, Federico Cilento *High repetition rate Time-Resolved VUV ARPES at 10.8 eV photon energy,* **arXiv:1911.05590 [physics.optics]**