Coherent two-dimensional photoelectron spectroscopy

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Introduction

Coherent multidimensional spectroscopy is a powerful ultrafast spectroscopic technique which provides information otherwise only accessible in disjunct experiments[1,2,3]. Another spectroscopic tool is photoelectron spectroscopy which provides detailed information about the chemical composition and electronic states of the sample by analyzing photoelectrons released from the sample[4].

Here we present a combination of both methods in a single experiment, realized with the implementation of efficient single-counting detection and multichannel software-based lock-in amplification[5]. The approach offers high temporal, spectral and kinetic energy resolution. It enables differential CMDS experiments with unprecedented selectivity and enhances the dynamic range of CMDS by up to two orders of magnitude. The demonstrated principle opens-up a perspective for atomically-resolved CMDS experiments using X-ray photoelectron spectroscopy.

Experimental Setup

The experiment is based on population-detected 2D electronic spectroscopy (2DES) combined with photoelectron spectroscopy.
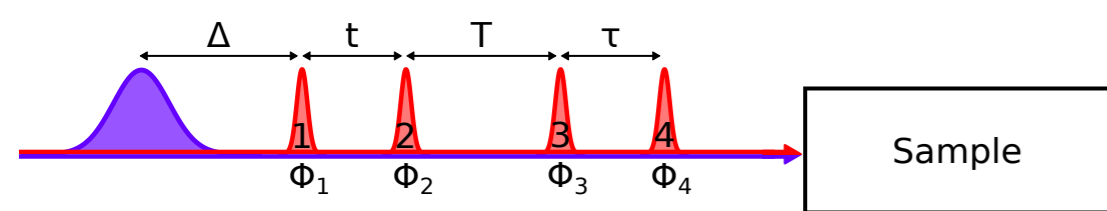
2D electronic spectroscopy

Figure adopted from [6].

The 2D electronic spectroscopy (2DES) signal is generated by a collinear sequence of 4 phase-modulated laser pulses. A fifth UV pulse ionizes the sample afterwards.

Coherent 2D photoelectron spectroscopy

We employ a special phase modulation technique combined with Lock-In detection, in order to extract the weak 2DES signal.
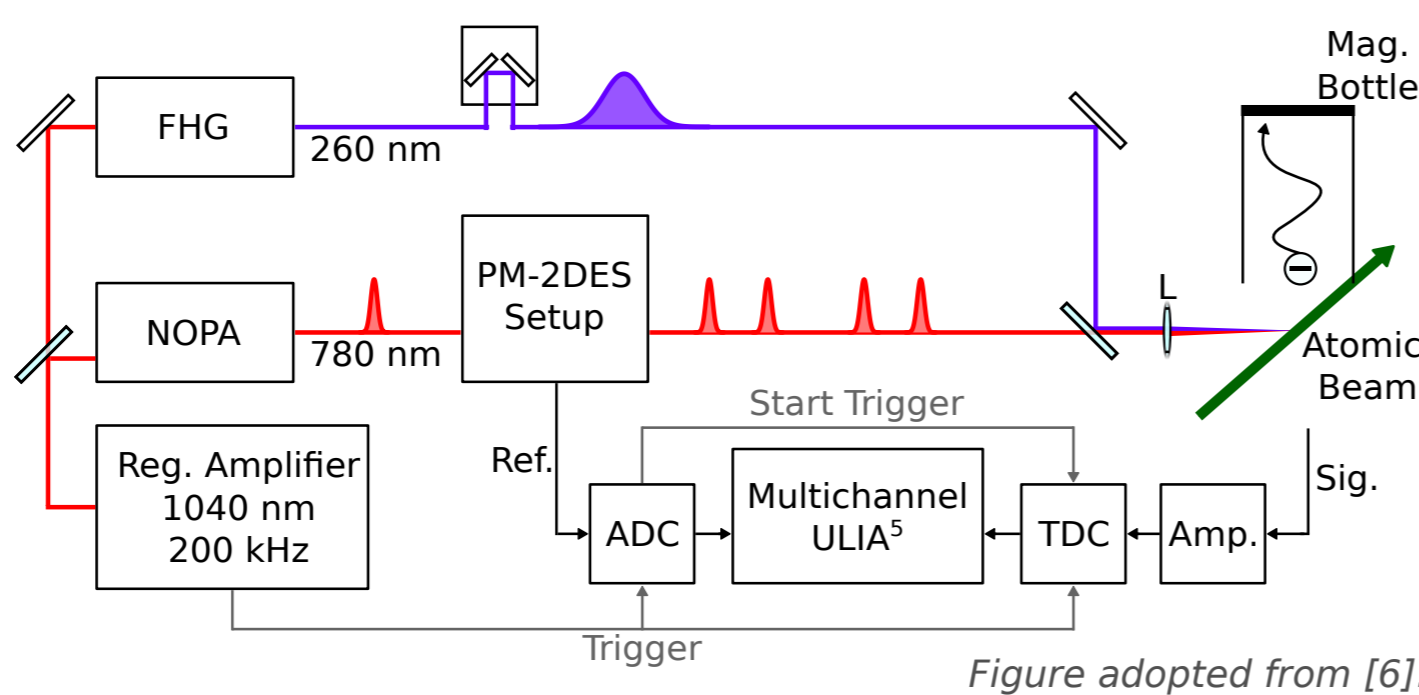

Figure adopted from [6].

The photoelectrons are detected by a magnetic bottle electron time-of-flight spectrometer. A time to digital converter analysis the flight times of the photoelectrons. With this the kinetic energy spectrum is reconstructed.
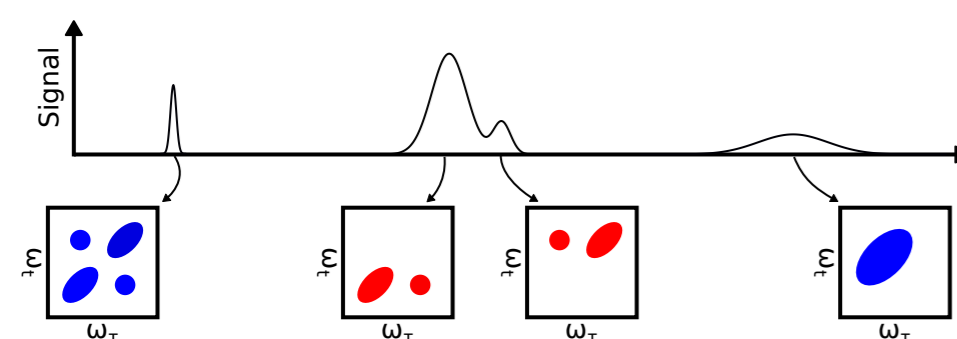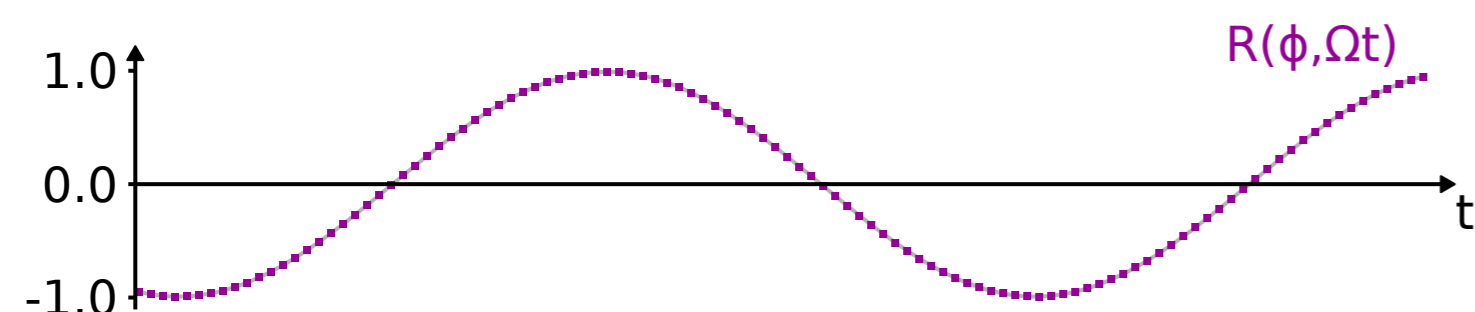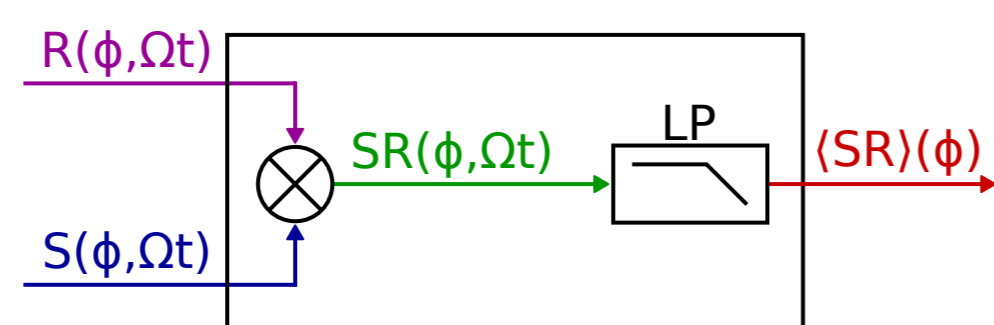

Figure adopted from [6].

The 2D spectra for a specific electron orbital are retrieved by demodulating the electron yield for a specific kinetic energy (KE).
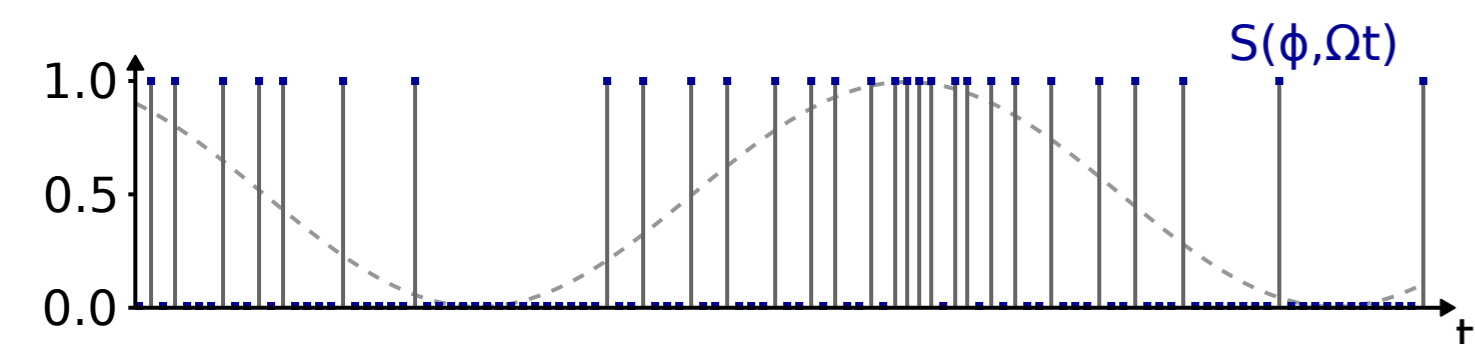
Single counting Lock-In amplification

Since standard Lock-In amplifier are not well suited to perform single counting detection, we developed a software-based universal lock-in amplifier[5].
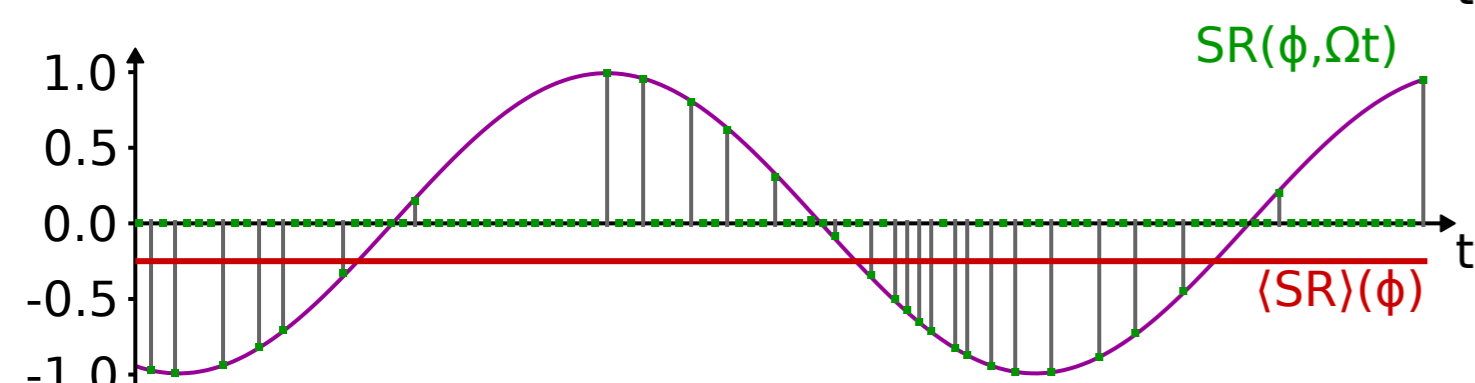

Basic principle of a Lock-In amplifier.

Reference signal acquired over multiple laser shots.

In this scheme the signal is amplitude-discriminated, the information is encoded in the count rate.

Multiplied signal in green and averaged (demodulated) signal in red.
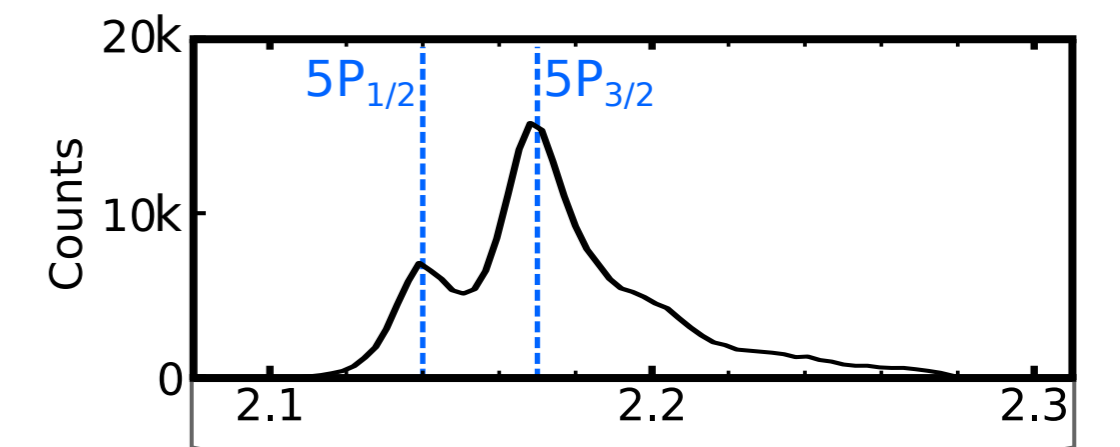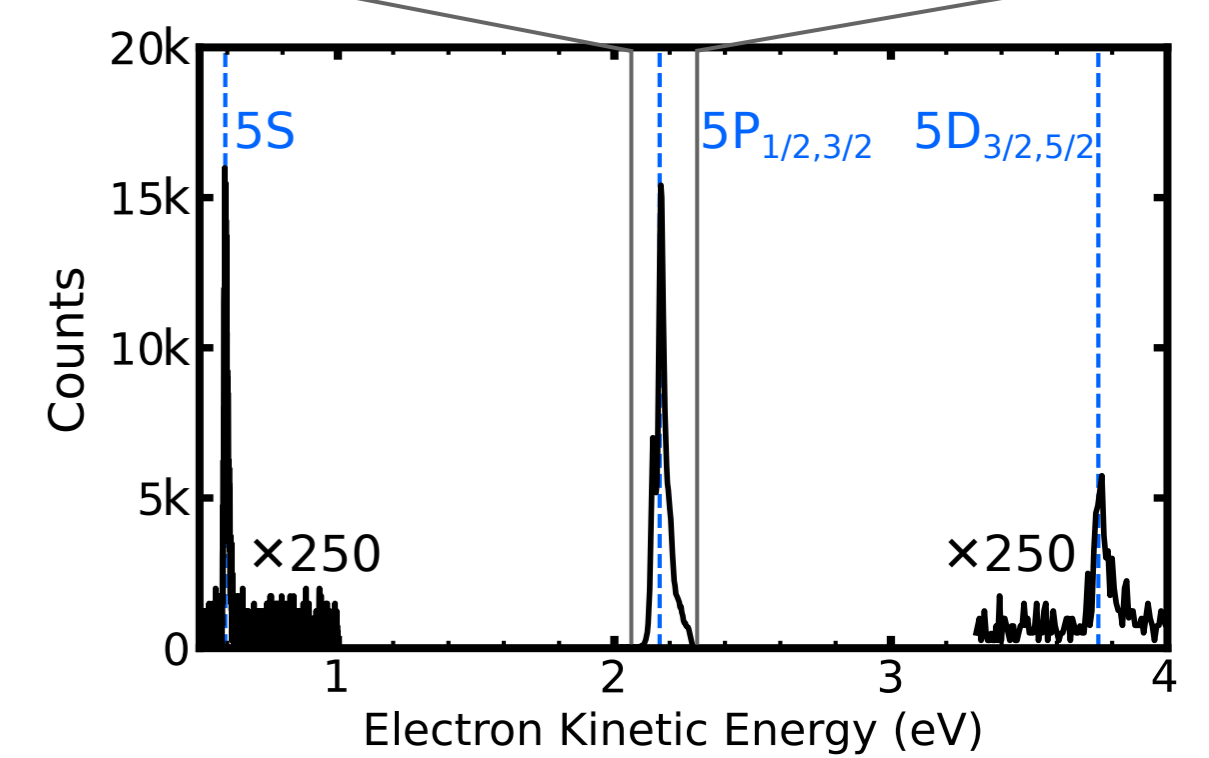
Figure adopted from [6].

Results

Photoelectron spectra

As a sample atomic rubidium is used in the here presented experiment.

Zoom on the x-axis of the 5P reveals a clear separation of the $5P_{1/2}$ and $5P_{3/2}$ states.


The complete photoelectron spectrum. With the configuration of our setup the 5S, 5P, and 5D can be resolved.

Note that the signal of the 5S and 5D is multiplied by a factor of 250 for visualization reasons.

Figure adopted from [6].

Differential 2D spectra

To demonstrate the capability of the differential detection scheme, 2D spectra were extracted from different regions of the photoelectron kinetic energy distribution and compared to the integral spectrum.

Figure adopted from [6].
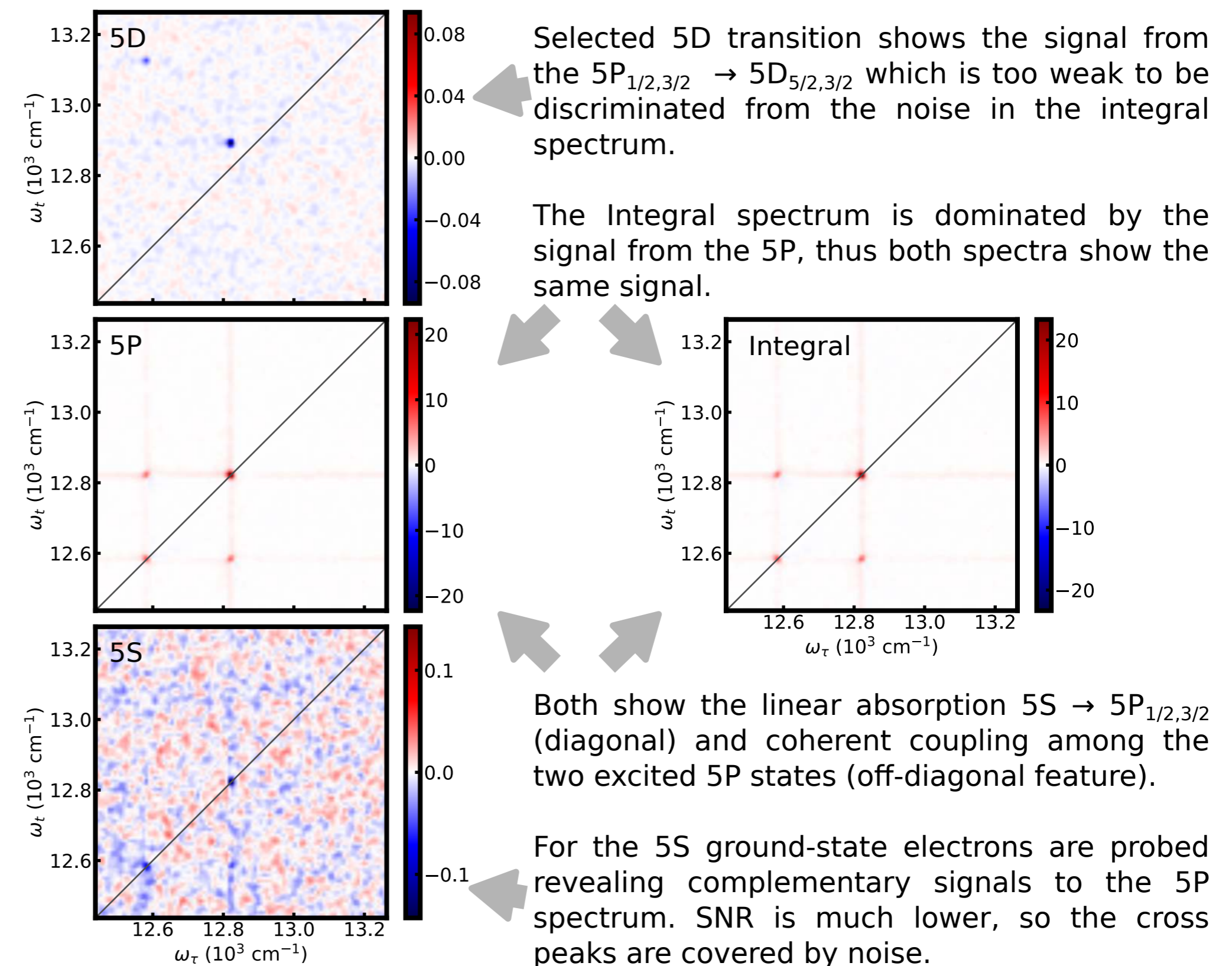
Selected 5D transition shows the signal from the $5P_{1/2,3/2} \rightarrow 5D_{5/2,3/2}$ which is too weak to be discriminated from the noise in the integral spectrum.

The Integral spectrum is dominated by the signal from the 5P, thus both spectra show the same signal.

Both show the linear absorption $5S \rightarrow 5P_{1/2,3/2}$ (diagonal) and coherent coupling among the two excited 5P states (off-diagonal feature).

For the 5S ground-state electrons are probed revealing complementary signals to the 5P spectrum. SNR is much lower, so the cross peaks are covered by noise.

Resolution Limit

To demonstrate the resolving power of photoelectron spectroscopy, we extracted differential 2D spectra from partially overlapping photoelectron peaks of the $5P_{1/2,3/2}$ states.
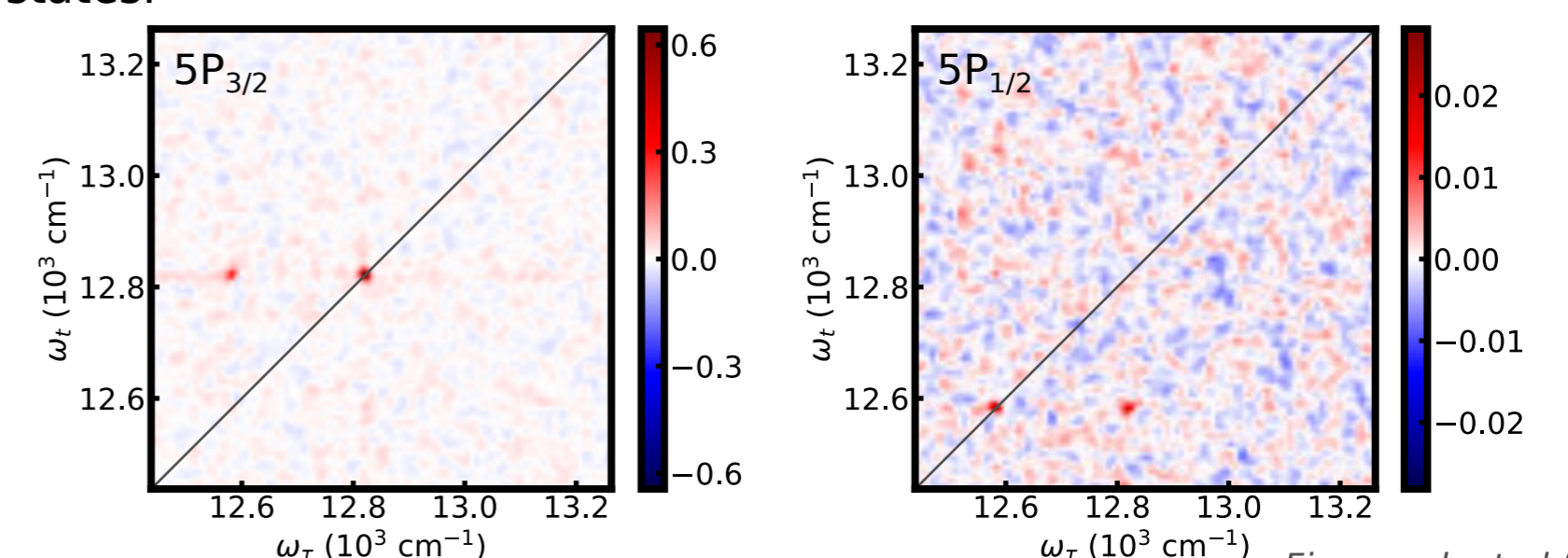

Figure adopted from [6].

References

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