# Delayed Core-Level Photoemission from the van der Waals Crystal WSe$_2$

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**Abstract:** Attosecond time-resolved XUV streaking experiments are reported for cleaved WSe$_2$ surfaces. The photoemission from Se 3d and W 4f core levels occurs delayed by 50 attoseconds with respect to the valence band emission.

OCIS codes: (320.7130) Ultrafast processes in condensed matter, including semiconductors; (270.6620) Strong-field processes; (240.6675) Surface photoemission and photoelectron spectroscopy; (340.7480) X-rays, soft x-rays, extreme ultraviolet (EUV);

## 1. Introduction

The availability of single attosecond (as) XUV pulses allows investigating ultrafast electron dynamics on the attosecond time scale. Photoelectron wavepackets generated by the XUV pulse are interacting with a simultaneously present IR streaking field. Measuring the photoelectron streaking for electrons emitted from different initial states as function of the delay between XUV and IR pulse allows determining the relative timing of the different emission processes. For a (110) tungsten surface Cavalieri et al. reported that the photoemission from tungsten 4f states is delayed by about 100 as with respect to the electron emission from the valence band [1]. The physical origin of this delay is not yet understood and controversial theoretical models coexist (for review see [2]). Recently, a study for Mg(0001) surfaces showed a vanishing delay between emission from Mg core levels and the valence band states [3] indicating that the degree of initial state localization has only minor influence on the photoemission dynamics. However, the identification of the physical mechanism responsible for the observed delays is obscured by the fact that a) the streaking field distribution at the interface is unknown on the atomic length scale, b) the photoelectron emission occurs over a depth regime of several Å and varies substantially for different final states, and c) any surface contaminations can easily alter the streaking effect. Hence, further attosecond time-resolved photoemission studies using other surfaces are needed to resolve the controversies related to the dynamics of the photoemission process. Here we report as-time-resolved photoemission from a van der Waals crystal that exhibits a completely different electronic structure compared to a bulk metal. The layered structure of the investigated solid yields element specific photoelectrons emitted from different but well defined depth and thus helps resolving the physical origin of temporal delays in photoemission. In addition, van der Waals crystals have rather inert surfaces and contamination effects are suppressed.
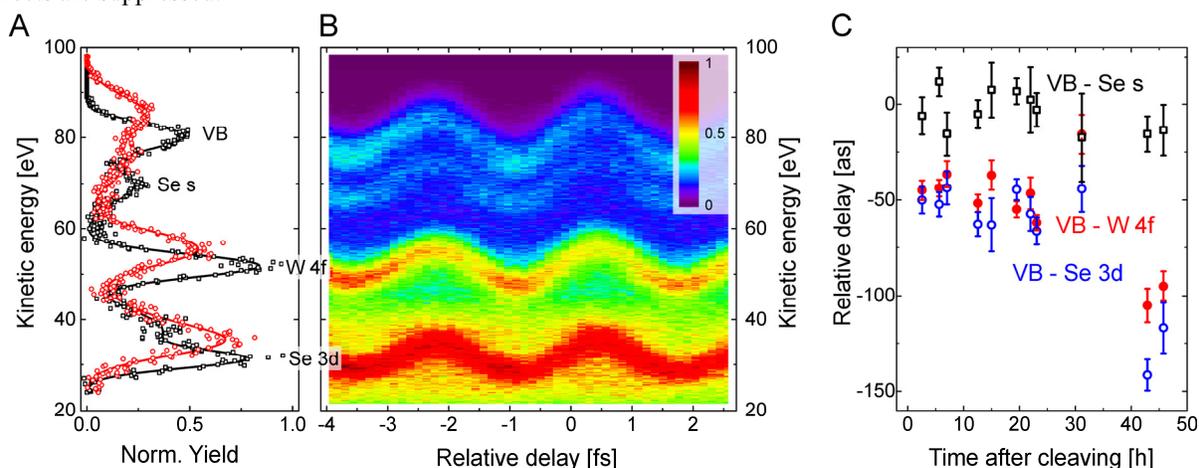


Fig. 1. Attosecond streaking from WSe$_2$ surface. A) Attosecond XUV photoemission spectra after background subtraction without acceleration (black) and with maximum accelerating (red). Solid lines represent multiple Gaussian fit curves. B) Contour plot of the photoemission spectra without background subtraction as function of delay between IR and XUV radiation. Positive delay indicates an earlier arrival of the XUV pulse. C) Delay of different photoemission contribution relative to the valence band emission as function of the time after cleavage.

## 2. Experimental setup

XUV pulses with about 300 as duration are generated by high harmonic generation (HHG) in a Ne target using 5 fs IR laser pulses with stable carrier-envelope phase in a setup that is similar to the one used for the W(110) experiment [1]. HH and IR radiation propagate collinearly and a multilayer X-ray mirror (peak reflectance at 91 eV, 6 eV bandwidth) is used to filter out an individual XUV pulse from the continuous HH spectrum in the cutoff. The X-ray mirror is mounted as movable inner mirror of a coaxial mirror assembly that superimposes XUV and IR radiation on the target (7° glancing angle) with variable delay. Photoelectrons emitted under normal direction are detected using a field-free time-of-flight setup. $WSe_2$ crystals are cleaved under UHV conditions ($10^{-10}$ mbar) and from the resulting pristine surface XUV photoemission spectra are recorded over one day without showing degradation. After background subtraction the recorded photoemission spectra are fitted with a series of Gaussian peaks and the obtained peak positions are used to determine the streaking effect for the different spectral contributions in the photoemission spectra.

## 3. Results and Discussion

The XUV photoemission spectrum is composed of a broad valence band emission centered at a kinetic energy $E_{kin}$ of 78.8 eV, the emission from a Se s-band at $E_{kin}$=70 eV, and the W 4f and Se 3d core level emission peaks at $E_{kin}$=51.7 eV and $E_{kin}$=31.1 eV, respectively. The feature appearing at $E_{kin}$=38eV is attributed to the filling of a Se 3d hole via a transition from Se s-band and related Auger electron emission from the valence band. From fitting the spectra recorded for different delay between IR and XUV pulse with a series of Gaussian peaks the energy positions of the various spectral components are determined. With exception of the Auger peak the photoemission components show pronounced streaking effects. The streaking effect for different initial states shows small phase shifts indicating that the electrons emitted by the attosecond XUV pulse experience the streaking field at slightly different times. The relative delay with respect to the emission from the valence band is determined by fitting the streaking curves. The obtained relative delays for 11 streaking measurements performed on 2 different samples for different times after cleaving the sample are summarized in Fig. 1C. Whereas there is no significant delay between the emission from the valence band and the Se s-band the photoelectrons from the Se 3d and W 4f are emitted with about 50 as delay. For about 30 h the behavior is unchanged indicating that surface contamination has no significant impact. For even longer exposure time the delay between core level and valence band emission increases. This increasing delay is explained by the growth of a surface contamination layer leading to longer transmission times of the photoelectrons emitted from core levels because of their lower kinetic energy compared to photoelectrons emitted from the valence band having the highest kinetic energy.

$WSe_2$ has a layered structure and each layer is composed of a single W layer sandwiched between two Se layers (± 1.67 Å apart). Neighboring W layers are separated by 6.48 Å and based on free electron propagation the emission from the second layer should be additionally delayed by about 150 as and 120 as for the W 4f and the valence band electrons, respectively, and 195 as and 130 as for the Se 3d and Se s-band electrons, respectively. No such delayed components can be identified in the streaking measurement and we therefore conclude that photoemission from the second $WSe_2$ layer is negligible. Thus, our measured 50 as delay between valence band and core level emission cannot be attributed to propagation effects. Because of the negligible role of surface contamination effects and the observation that the photoemission occurs from a single $WSe_2$ layer we conclude that properties of the photoemission initial and final states determine the observed delay. The created continuum electron wave packets originating from either localized core levels with different angular momentum or delocalized valence band states propagate in different effective potentials. As it was proposed in [4] this relates to relative phase shifts experimentally determined by means of spin-resolved photoemission and corresponding time delays that are accessible by means of attosecond time-resolved photoemission spectroscopy.

## 4. References

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