Attosecond-resolved petahertz carrier motion in semi-metallic TiS$_2$

Bárbara Buades$^1$, Antonio Picón$^{1,2}$, Iker León$^1$, Nicola Di Palo$^1$, Seth L. Cousin$^1$, Caterina Cocchi$^3$, Eric Pellegrin$^4$, Javier Herrero Martin$^4$, Samuel Mañas-Valero$^5$, Eugenio Coronado$^5$, Thomas Danz$^6$, Claudia Draxl$^1$, Mitsuharu Uemoto$^7$, Kazuhiro Yabana$^1$, Martin Schultze$^8$, Simon Wall$^1$, Jens Biegert$^{1,9,*}$

$^1$ICFO-Institut de Ciencies Fotoniques, The Barcelona Institute of Science and Technology, 08860 Castelldefels (Barcelona), Spain
$^2$Grupo de Investigación en Óptica Extrema, Universidad de Salamanca, Salamanca E-37008, Spain
$^3$Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany
$^4$ALBA Synchrotron Light Source, E-08290 Cerdanyola del Vallès, Barcelona, Spain
$^5$Instituto de Ciencia Molecular (ICMol), Universitat de València, Paterna, Spain
$^6$4th Physical Institute - Solids and Nanostructures, University of Göttingen, Göttingen, Germany
$^7$Center for Computational Sciences, University of Tsukuba, Tsukuba 305-8577, Japan
$^8$Fakultät für Physik, Ludwig-Maximilians-Universität, Am Coulombwall 1, D-85748 Garching, Germany
$^9$ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain
$^*$Correspondence to: jens.biegert@icfo.eu

Knowledge about the real-time response of carriers to optical fields in solids is paramount to advance information processing towards optical frequencies or to understand the bottlenecks of light-matter interaction and energy harvesting. Of particular importance are semi-metals and transition metal dichalcogenides due to their small band gap and high carrier mobility. Here, we examine the opto-electronic response of TiS$_2$ to optical excitation by means of attosecond soft x-ray spectroscopy at the L-edges of Ti at 460 eV. Using weak-field infrared single-photon excitation, we examine conditions that avoid excessive excitation, but still attain efficient injection of 0.2% of valence band carriers into the lowest lying conduction band. We demonstrate that the efficient injection and the high-carrier mobility of the conduction band permits leveraging the material to achieve petahertz-speed opto-electronic control of its carriers. Our results are an important step towards understanding the dynamics of carriers and their control under field conditions that are realistic for device implementation in semi-metallic layered materials, thus they may lead to ultrafast and optically controlled field-effect devices and sensors.

The distribution and real-time motion of charge carriers close to the Fermi level is of fundamental importance since these carriers predominantly determine the optical and electronic properties of a material and thus the functionality of devices composed of it. Especially relevant in this context are layered quantum materials for which Titanium Disulfide (TiS$_2$) is a paradigmatic example being a semi-metallic transition-metal dichalcogenide (TMD) compound, with attractive structural and electronic properties. For instance, its electron mobility ranges between that of a metal and a semiconductor, which, together with its high ion mobility, render TiS$_2$ of interest as platform for ultrafast optoelectronic devices and field-effect transistors, and for solid batteries and high-density energy storage. Advancing on these prospects ultimately calls for a deeper understanding of the non-equilibrium dynamics of carriers in the conduction band, closest to the Fermi level, in real time and in the presence of an electric control field that is weak enough to be achievable in devices, e.g. with plasmonic nano-focusing. To study such aspects in materials, thus far, a range of ground-breaking experiments have employed absorption spectroscopy with atto- to femtosecond resolution and investigated the ultrafast response of semiconductors and insulators under strong field excitation, and with carriers injected into high-lying conduction band states. Here, in contrast, the aim was to elucidate the dynamics of carriers of semi-metallic TiS$_2$ close to the Fermi level by means of single-photon excitation. The challenge for element-selective
investigations of TMDC’s is accessing the d-character conduction band states, which translates into the necessity for attosecond spectroscopy at soft x-ray photon energies to leverage the dipole-allowed L-edge core transitions of the transition metal atoms. Here, we meet this challenge through a first investigation of the non-equilibrium dynamics of conduction band charge carriers close to the Fermi level, with a weak infrared optical control field in the TMDC TiS$_2$, interrogated with attosecond temporal resolution.

The attractive properties of TiS$_2$ arise from its tri-layered structure, shown in Fig. 1a, which consists of hexagonal sheets of cationic Ti$^{4+}$(3d$^2$) atoms sandwiched between sheets of sulfur atoms. The atoms within the tri-layers (S-Ti-S) are covalently bonded while the tri-layers are coupled by Van der Waals forces, resulting in physical properties that are anisotropic to an extent that the material can be regarded as quasi-two-dimensional solid$^3$. Moreover, the material’s band structure changes only marginally when reducing dimensionality to the monolayer$^4$. Figure 1b shows the semi-metallic band structure of bulk TiS$_2$ calculated from first principles in the framework of density-functional theory (DFT); see supplementary materials. The angular momentum character of the valence bands originates from mixed sulfur 3p and 3s states, while the conduction bands are predominantly of titanium 3d character.

![Soft X-ray absorption spectroscopy in TiS$_2$.](image)

**Fig. 1** Soft X-ray absorption spectroscopy in TiS$_2$. a The sub-2-cycle 1.85-μm (0.6 eV) pump pulse stimulates carrier dynamics inside a 150-nm-thin TiS$_2$ crystal (sketched are two layers), which is probed by a 300-as-duration SXR pulse at 30 degrees to the material’s basal plane normal. b shows the relevant band structure of the TiS$_2$ semimetal together with IR induced excitation pathways and the accessible core transitions. The attosecond SXR pulse invokes L$_2$ transitions from titanium 2p core orbitals into conduction band states which are predominantly of Ti-3d character. c shows the attosecond absorption spectrum of the un-pumped material with both, Ti L$_2$ and L$_3$ edges resolved.

To investigate the dynamics of carriers in the lowest conduction band states, we employed x-ray absorption spectroscopy with isolated 300-as-duration soft x-ray (SXR)$^{28,29}$ pulses. The attosecond pulse spectrum contains photon energies ranging from 200 to 550 eV, thus accessing the titanium 2p core states at -458.4 eV ($2p_{3/2}$) and -465.5 eV ($2p_{1/2}$); see Fig 1b. These x-ray initiated L-edge core transitions allow then to directly interrogate the material’s 3d-character conduction band states via x-ray absorption near-edge structure (XANES) spectroscopy$^{30,31}$. Shown in Fig. 1c is the XANES together with its derivative ($\partial \text{OD}/\partial E$) to identify the positions of the Ti L$_2$ and L$_3$ absorption edges that arise due to transitions from 2p$_{3/2}$ and 2p$_{1/2}$ core states. The static XANES measurement, i.e. un-pumped and non-time-resolved, serves as reference and it is in excellent agreement with a measurement at the synchrotron light source ALBA and well reproduced by theory (see supplementary materials).

The opto-electronic response of the material was interrogated by applying an optical control field at a photon energy of 0.6 eV. This optical field could thus directly bridge the 0.23 eV separation of valence and conduction band between the Γ and A points via single-photon excitation whilst avoiding excitation of high-lying conduction bands. The control field was a carrier-envelope-phase (CEP) stable, 1.8-cycle-duration (12 fs FWHM) laser pulse at a center wavelength of 1850 nm and a low-energy replica of the pulse that produced the isolated attosecond SXR pulse through high harmonic generation. The peak intensity of the control field was $(4.1 \pm 0.8) \times 10^{11}$ W/cm$^2$, corresponding to an electric field amplitude of 0.08 V/Å inside the
material, and excited approximately 0.03 electrons per unit cell. An important aspect to resolve the material response on the scale of the electric field waveform of the control field is, in addition to the SXR pulse attosecond duration, a fast core-hole decay of the material. The core hole decay of the Ti 2p states of 2.3 fs is faster than the cycle period of the control field (one optical cycle equals 6.1 fs at 0.6 eV), which permits to fully leverage the attosecond SXR pulse’s time resolution to resolve carrier dynamics on the sub-cycle scale of the optical control field. In the experiment, the SXR attosecond probe interrogated a 150-nm-thick, free-standing, mono-crystalline 1T-TiS₂ sample at 26-degrees incidence with respect to the basal plane normal to sample the entire k-space of the conduction band. A 20-micron-thick nickel disc of 3-mm outer diameter and with a central hole of 100-micron diameter was positioned on top of the TiS₂ sample to define the area of spatial overlap between the attosecond probe and the infrared control field. The measurement was taken with a home-built spectrometer consisting of a reflective 2400 l/mm Hitachi grating and cooled CCD-camera (PIXIS, Princeton Instruments) for readout.

**Fig. 2a | Time-resolved dynamic in TiS₂. a** Differential absorption spectrum as a function of pump-probe delay. ΔT is normalized to the un-pumped case T₀ for each time delay. Clearly visible are sub-cycle oscillations of negative and positive differentials with amplitude of 10%. Time delays were 100 as for negative delays to -5 fs with 6 min integration and 200 as steps with 5 min integration elsewhere. b shows spectral lineouts from a, taken at the positive and negative extrema (spectral oscillations). The dynamics, red for increased and green for diminished ΔT in relation to the absorption edge, c indicates the optical control field. d displays the relevant subsection of a for comparison with the cBE calculated differential absorption in e. f overlays the measurement with the theoretical result, indicating good agreement. g shows the calculated carrier excitation with both models, cBE and RT-TDDFT.

Figure 2a shows the differential absorption spectrum (ΔT = Tₚumped − T₀) normalized to the unpumped case (T₀), as a function of IR-pump, attosecond-SXR-probe delay. Negative time values correspond to the SXR probe arriving before the IR control field, and a positive (red) value reports an increasing SXR transmission due to the field-induced excitation of the material, thus a decrease in carrier population in Ti-3d conduction band states. Immediately apparent in the measurement is a transient signal with an amplitude of 10%, at twice the oscillation frequency of the IR optical field, and which exhibits oscillations with excursions to both, positive (red) and negative (blue), values. Fig. 2b depicts lineouts of the differential absorption (Fig. 2a) at different time delays and establishes that the control-field-induced carrier dynamics indeed occurs at the bottom of the Ti-3d conduction band, closest to the Fermi level.

To obtain detailed physical insight into the underlying carrier dynamics in TiS₂, we turned to theory. We performed a first-principles electron dynamics simulation of the full pump-probe experiment based on real-time time-dependent density functional theory (RT-TDDFT)². In addition to the ab-initio model, we developed a core-state-resolved Bloch equation model (cBE) to examine the various concurrent inter- and intra-band contributions in response to the control field. The cBE model retains the relevant five bands in three dimensions; it includes the three highest-occupied valence and two-lowest-occupied conduction band states together with the Ti-2p core states. Details on the theories and simulations are given in the supplementary materials. The result of the cBE simulation, including the full inter- and intra-band dynamics,
is shown in Fig. 2e. The good qualitative match between the measurement (Fig. 2a and d) and calculations (Fig. 2e) is further confirmed in Fig. 2f, which shows the differential absorption integrated over an energy interval of 5 eV where the changes are most prominent (between 457 and 462 eV). Indicated in Fig. 2c is the IR control field periodicity which shows that carriers response (Figs. 2d-f) occurs on the sub-cycle temporal scale with oscillations at twice the control field frequency (2ω_f). The origin of the 2ω-oscillation has been previously discussed as originating from the ac Stark effect which modulates the optical absorption (Dynamic Franz Keldysh effect26,27) due to the external pump field for tunneling-type optical excitation.

In particular, the cBE model enables us to disentangle the different signatures of resonant and off-resonant contributions to the absorption, including bandgap renormalization. Interestingly, our investigation shows that inter-band transitions are predominantly of non-resonant character despite a low field strength and photon energies which can directly bridge the gap between valence and conduction bands; e.g. at the Γ point the gap is 0.23 eV. We attribute this result to the large spectral bandwidth of the short-duration excitation pulse which accesses a much higher density-of-states (DOS) in the valence bands through non-resonant inter-band transitions compared to a relatively small DOS via resonant inter-band transitions. This is an exciting finding for a semimetal, since, despite gap energies in TiS_2 of around 0.23 - 4 eV and a Keldysh parameter of 2.5, the optical response is governed by a non-resonant transition scenario analogous to a semiconductor or dielectric material22,26. Thus, this may provide opportunities to leverage the high carrier mobility of the semimetal whilst operating the material with aspects similar to a semiconductor. Having elucidated the nature of the inter-band transition, we used both models to predict the magnitude of injection of carriers into the conduct band. Shown in Fig. 2g is the result from a projection of the time-dependent wavefunction of the five-band cBE and from the RT-TDDFT models onto the conduct band states. We find very good agreement amongst the simulations with a predicted value of -0.2%.

**Fig. 3 | Inter & Intra-band contributions.** Calculated material response from the 5-band cBE model. Displayed is a decomposition of the differential absorption spectrum as a function of pump-probe delay; all plots are log(ΔT/ΔT_0). a shows the total contribution, including inter- and intra-band carriers, to the absorption spectrum which consists of time-varying Fano absorption profiles. b and c show the inter- and intra-band contributions to a. The intra-band contribution displays excursions to both positive and negative absorption values, while the inter-band contribution reaches only positive values. Moreover, the inter-band contribution is one order of magnitude weaker than the intra-band contribution. Thus, the material response is predominantly governed by intra-band motion of carriers.

To further investigate carrier dynamics in TiS_2, we elucidate the role of inter- and intra-band carrier dynamics and how it can be inferred from the measured absorption spectrum. In general, the transfer of electrons to the conduction band at a specific k-space position results in Pauli blocking and, since the core-level transition (Ti-2p to Ti-3d) accesses conduction band states, this leads to bleaching of the SXR absorption. Equally vital is the role of intra-band motion of carriers as, depending on the mobility, it may diminish (or increase) Pauli blocking at a particular k-space position (e.g. the Γ point), hence act to modify the SXR absorption. It is worth emphasizing that we specifically chose conditions with a low field strength of 0.08 V/Å and Keldysh parameter of 2.5 for which Rabi cycling between the valence and conduction bands is negligible, thus permitting to investigate the influence of the TMDC’s high carrier mobility to the dynamics. Figure 3 shows results from a high-resolution cBE calculation based on the ~0.2% injection of carriers into the conduction bands. Immediately visible in Fig. 3a is the ubiquitous 2ω-oscillation to both, positive and negative values, in addition to time-dependent line-shape modification due to the time-evolution of the optical control field. The oscillation pattern arises from an interplay of contributions, predominantly due to injection of valence
band carriers, in addition to a small contribution - on the order of 0.01% - of core electrons with an accumulated dipole-phase acquired during the excitation into the conduction band, analog to atomic physics experiments\textsuperscript{33,34}. Further, contrasting inter-band (Fig. 3b) with intra-band (Fig. 3c) contribution shows that intra-band motion dominates over inter-band motion by one order of magnitude. Interestingly, the oscillation to both positive and negative values originates only from intra-band carriers, thus emphasizing their very high mobility and confirming the absence of Rabi cycling.

To summarize, our measurements investigate the opto-electronic response of the semi-metallic TMDC TiS\textsubscript{2} to petahertz control fields. In contrast to previous investigations, our weak-field and single-photon excitation conditions leverage the high mobility of TiS\textsubscript{2} and demonstrate its enticing prospects to inject a significant fraction of carriers and to control their intra-band motion entirely with the same control field with petahertz velocity. Our simulations describe the experimental measurements, thus permit elucidating the magnitude and interplay of inter-band and intra-band contributions to the carrier dynamics mediated by the optical control field. Our investigation of the prototypical TMDC TiS\textsubscript{2} provides important information on the usage of semimetals and TMDCs as building blocks, such as “light-valves” or field effect transistors, for the next generation of opto-electronic devices and light-wave electronics.
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