Two-photon IR pumped UV-Vis transient absorption spectroscopy of Dirac fermions in the 2D and 3D topological insulator Bi$_2$Se$_3$

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It is often taken for granted that in pump-probe experiments on the topological insulator (TI) Bi$_2$Se$_3$ using IR pumping with a commercial Ti:Sapphire laser [~800 nm (1.55 eV photon energy)], carriers are excited in the one-photon absorption regime, even when pumped with absorbed fluences in the mJ cm$^{-2}$ range. Here, using UV-Vis transient absorption (TA) spectroscopy, we show that even at low-power IR pumping with absorbed fluences in the μJ cm$^{-2}$ range, TA spectra of the 2D and 3D TI Bi$_2$Se$_3$ cover the entire visible and part of the UV region. This observation unambiguously indicates that the two-photon pumping regime accompanies the common one-photon pumping regime even at low laser powers applied. We attribute the high efficiency of two-photon pumping to the giant nonlinearity of Dirac fermions in Dirac surface states (SS). On the contrary, one-photon pumping is associated with the excitation of bound valence electrons in the bulk into the conduction band. We also identified two mechanisms of absorption bleaching, which manifest themselves in different spectral regions of probing and are associated with direct Pauli blocking in Dirac SS and an integrated filling of the phase-space in the bulk states. The effect of the film thickness and pumping power on the mass gain/loss dynamics of Dirac fermions upon relaxation and their vertical transport, as well as on the launching of coherent longitudinal optical (LO) phonon oscillations in the bulk states and Dirac SS is demonstrated. We have shown that the launching of coherent LO-phonon oscillations in the bulk is governed by the vertical electron transport, while the coherence of LO-phonon oscillations in Dirac SS is provided by an in-phase sequential scattering of Dirac fermions from the uppermost atomic layer of the surface.

I. INTRODUCTION

Since the discovery of 3D topological insulators (TIs)\textsuperscript{1,3}, the energy relaxation dynamics of photoexcited carriers in these materials has been extensively studied during the last decade or so using a variety of pump-probe techniques exploiting ultrashort IR pumping with a commercial Ti:Sapphire laser [~800 nm (1.55 eV photon energy)].\textsuperscript{4,22} Specifically, time-resolved and angle-resolved photoemission spectroscopy (TrARPES),\textsuperscript{4,9} pump-probe reflectivity,\textsuperscript{10,15} pump-probe second harmonic generation (SHG),\textsuperscript{11,16} pump-probe X-ray diffraction,\textsuperscript{17} transient reflectivity spectroscopy,\textsuperscript{18,20} and transient conductivity spectroscopy\textsuperscript{21,22} were used for these purposes. It is important to note that only in the TrARPES experiments both two-photon photoemission and ordinary one-photon photoemission were considered as the probing methods.\textsuperscript{9} On the contrary, IR pumping at Ti:Sapphire laser wavelengths was usually assumed to occur in the one-photon absorption regime for all pump-probe experiments, even if carriers were pumped at high powers with absorbed fluences in the mJ cm$^{-2}$ range.\textsuperscript{11,16,17} However, recent applications of transient absorption (TA) spectroscopy to study ultrathin Bi$_2$Se$_3$ films have clearly demonstrated that for this carrier excitation regime, two-photon pumping of massless Dirac fermions in Dirac surface states (SS) must also be considered on a par with an one-photon pumping of bound valence electrons in the bulk states.\textsuperscript{25} Moreover, the relaxation dynamics observed for Dirac SS using two-photon IR pumping turned out to be very close to that observed with the corresponding one-photon UV pumping,\textsuperscript{24} thus unambiguously confirming the reality of two-photon excitation.

In this paper, we present a thorough study of relaxation dynamics of Dirac fermions and electrons, including their mass gain/loss dynamics upon relaxation, in the 2D and 3D TI Bi$_2$Se$_3$ using TA spectroscopy exploiting low-power IR pumping with absorbed fluences in the μJ cm$^{-2}$ range. The corresponding film thicknesses were 2 and 10 quintuple layers (QL) stacked together by van der Waals interaction (~2 and ~10 nm, respectively), where QL represents five covalently bonded Se-Bi-Se-Bi-Se atomic sheets. All measurements were carried out under ultrashort (~100 fs) pumping at a wavelength of ~730 nm (photon energy ~1.7 eV) and probing in the UV-Vis region (1.65 - 3.8 eV). We have shown that even at low pumping power, TA spectra cover the entire visible and part of the UV region, thus clearly indicating the two-photon pumping regime. We associate the high efficiency of two-photon pumping with Dirac fermions. This conclusion is hence in good agreement with the giant nonlinearity of 2D Dirac systems, which exhibit an extremely strong nonlinear optical response.\textsuperscript{25,26}
Analyzing the corresponding pump-probe traces as a function of probing photon energy, we also identified two mechanisms of absorption bleaching (AB), which appear in different spectral regions. We associate them with direct Pauli blocking in Dirac SS and an integrated filling of the phase-space in the bulk states. We also have shown that since the TI Bi$_2$Se$_3$ is a van der Waals system, the coherent longitudinal optical (LO) phonon oscillations observed in the AB traces of the 3D TI Bi$_2$Se$_3$ are caused by the vertical electron transport, which spatially synchronizes the electron-LO-phonon scattering events in individual QLs. As the vertical electron transport in the 2D TI Bi$_2$Se$_3$ becomes negligible, the coherent LO-phonon oscillations in the AB traces disappear, whereas they emerge in the pump-probe traces associated with the inverse bremsstrahlung type free carrier absorption (FCA) in Dirac SS. The launching of coherent LO-phonon oscillations in Dirac SS is caused by the in-phase successive scattering of Dirac fermions from the uppermost atomic layer of the surface. Finally, we concluded that the two-photon IR pumped UV-Vis TA spectroscopy of Dirac fermions is a powerful and selective tool for studying ultrafast relaxation dynamics in 2D Dirac systems.

II. EXPERIMENTAL DETAILS

A. Sample preparation.

The 2 and 10 nm thick Bi$_2$Se$_3$ films were grown on 0.5 mm Al$_2$O$_3$(0001) substrates by molecular beam epitaxy, with a 10 nm thick MgF$_2$ protecting capping layer, which was grown at room temperature without exposing the film to the atmosphere. The samples have been found to be epitaxial and the nominal number of QL was accurate to approximately 5%. The level of disorder of the grown films and their quality were approximately the same.

Furthermore, the films reveal the thickness-dependent $n$-type doping with the free carrier density of ~10$^{19}$ cm$^{-3}$. 28

B. Experimental setup.

TA spectra were measured using the TA spectrometer (Newport), which was equipped with a Spectra-Physics Solstice Ace regenerative amplifier (~100 fs pulses at 800 nm with 1.0 kHz repetition rate) to generate the supercontinuum probing beam and a Topas light converter for the pumping beam. The spectrometer has also been modified to suppress all coherent artifacts emanating from the sapphire substrates and appearing on a subpicosecond time scale. We used optical pumping at 730 nm (1.7 eV photon energy) and a supercontinuum probing beam generated in a sapphire plate and spread across the UV-Vis spectral region from ~1.65 to ~3.8 eV. The probing beam was at normal incidence, while the pumping beam was at an incident angle of ~30°. All measurements were performed in air and at room temperature using a cross-linear-polarized geometry. Specifically, the pumping and probing beams were polarized out-of-plane (vertical) and in-plane (horizontal) of incidence, respectively. The data matrix was corrected for the chirp of the supercontinuum probing pulse and the zero-time was adjusted in each measurement using the coherent signal from a thin (0.3 mm) sapphire plate.

The spot sizes of the pumping and probing beams were ~400 and ~150 μm, respectively. The pumping beam average power was ~0.5 mW, which corresponds to the pumping intensity (power density) of ~4.0 GW cm$^{-2}$. The higher power pumping of ~3.0 mW (~27 GW cm$^{-2}$) was used for comparison with previously measured data. 23 We will refer these two pumping regimes further below to as the low-power and high-power pumping regimes.

Because one-photon absorption in the bulk states and two-photon absorption in Dirac SS occur simultaneously, the attenuation of the initial light intensity ($I_0$) propagating the distance $z$ through the Bi$_2$Se$_3$ film can be expressed as

$$\frac{\partial I(z)}{\partial z} = -\alpha I_0(z) - \beta I_0^2(z),$$

(1)

where $\alpha$ and $\beta$ are the linear (one-photon) and nonlinear (two-photon) absorption coefficients for the bulk states and Dirac SS, respectively. However, these two contributions seem to be indistinguishable due to the extreme thinness of Dirac SS. It is worth noting that owing to this two-component behavior, the effective linear absorption coefficient that was measured for thin Bi$_2$Se$_3$ films has revealed a ~2-fold increase with decreasing film thickness from ~40 to ~6 nm. 13 Subsequently, this increase in the linear absorption coefficient has been found to be in good agreement with an increase in the free carrier density measured for the same samples using the Hall effect. 28 This correlation between the free carrier density increase and the linear absorption enhancement with decreasing film thickness unambiguously suggests that the two-photon absorption is actually associated with the free carrier population initially residing in Dirac SS due to natural $n$-doping. As a result, we will use the effective linear absorption coefficient to estimate the corresponding absorbed fluences, instead of taking into consideration the simultaneously acting one-photon and two-photon absorption. Despite the imperfection of this procedure, it seems appropriate if we assume the comparable rates of one-photon and two-photon absorption.

The corresponding absorbed fluences for the low-power and high-power pumping regimes were estimated using the pumping light absorbivity ($A = 1 - R - T$), reflectivity ($R$), and transmissivity ($T$) at ~0.21 m$^2$ cm$^{-2}$ and ~1.0 m$^2$ cm$^{-2}$ for the ~10 nm thick film and at ~16 μJ cm$^{-2}$ and ~27 μJ cm$^{-2}$ for the ~2 nm thick film. Here we used the following measured parameters: the effective linear absorption coefficient of $\alpha = 1.9 \times 10^5$ cm$^{-1}$ and $1.2 \times 10^6$ cm$^{-1}$, as well as the reflectivity of $R = 0.25$ and ~0.2, for the 10 and 2 nm thick films, respectively. 13 We note that the calculated fluences for the low-power pumping regime are slightly higher than those used in the TrARPES and some pump-probe reflectivity experiments, 14-19 whereas they are comparable or even lower those used in the pump-probe measurements exploiting SHG, conductivity, and X-ray as the probing methods. 11,16-17,22 The broadband probing beam was of ~0.4 mW average power, which for the same as the pumping beam bandwidth (~26 mV) provides the probing intensity of ~0.15 GW cm$^{-2}$. Because the latter value is much smaller than that of the pumping beam, the probing beam effect on carrier excitation seems to be negligible.

III. RESULTS AND DISCUSSION

A. TA spectra of 2 and 10 QL thick Bi$_2$Se$_3$ films.

TA spectra of the 2 and 10 nm thick Bi$_2$Se$_3$ films, presenting the 2D and 3D TI Bi$_2$Se$_3$, respectively, which were measured using the low-power pumping regime, are extended from ~1.65 to ~3.8 eV [Fig. 1(a), (b) and (c), (d)]. This broadband contribution gradually develops on a subpicosecond time scale. The observed TA spectra of the 2D TI Bi$_2$Se$_3$ consists of negative and positive contributions, while only negative contributions appear for the 3D TI Bi$_2$Se$_3$. These spectral features are fully consistent with those previously reported for more powerful pumping. 23 Specifically, the
A positive contribution is known to be due to the inverse bremsstrahlung type FCA in the Dirac SS2, while the negative contributions are associated with the conduction band (CB) AB (the broadband negative contribution) and the valence band (VB) AB (the narrow negative contribution peaked near the pumping photon energy) [Fig. 1(e)]. Since the broadband contribution significantly exceeds in energy the pumping photon energy, it clearly points to the two-photon pumping of Dirac fermions, initially located in the upper cone of the Dirac SS1 below Fermi energy \(E_F\), toward the higher energy Dirac SS4. The two-photon excitation transition is expected to occur resonantly due to direct optical coupling between the Dirac SS1 and the Dirac SS2. Further relaxation of two-photon-excited Dirac fermions governs a broadband AB contribution, which expands from the initial two-photon excitation energy of Dirac fermions (2×1.7 eV + \(E_F\)) toward the lower energy bulk states and Dirac SS that are successively filled upon relaxation. However, two-photon pumping occurs simultaneously with the one-photon pumping of the bound valence electrons in the bulk. The latter process causes two relaxation dynamics. Specifically, one-photon-excited electrons additionally contribute to the CB-AB response, as discussed in the next section. Alternatively, the one-photon-excited holes block out the probing optical transitions originating in nearly the edge of the VB and the lower Dirac cone of the Dirac SS1. The resulting narrow VB-AB contribution characterizes the slow (nanosecond/microsecond range) relaxation of one-photon-excited holes in the bulk.
Although a decrease in pumping power has little effect on the shape of TA spectra for the 3D TI Bi$_2$Se$_3$, the CB-AB contribution for the 2D TI Bi$_2$Se$_3$ significantly increases, while the FCA contribution weakens and its higher energy edge shifts to lower energies with decreasing pumping power. The latter trends indicate that both contributions are caused by the density of photoexcited carriers, which are redistributed between Dirac SS and the bulk states. Consequently, the relaxation dynamics in the 2D TI Bi$_2$Se$_3$ tends to include the bulk states to a greater extent with decreasing pumping power. On the contrary, with an increase in pumping power, relaxation through Dirac SS manifests itself more significantly. This type of carrier redistribution is typical for ultrathin Bi$_2$Se$_3$ films and was also observed under UV pumping.

The discussed redistribution of two-photon-excited Dirac fermions between Dirac SS and the bulk states upon relaxation also manifests itself through the relaxation rates [Fig. 1(f) and (g)]. In particular, the dynamics of relaxation exhibits a two-stage behavior, which is characterized by the corresponding rates of ~1.7 and ~3.5 eV ps$^{-1}$. The difference in rates is associated with quasi-elastic and inelastic electron-phonon interactions in Dirac SS and the bulk states, respectively. Furthermore, the partial contribution of the rate characterizing the relaxation of Dirac fermions in Dirac SS increases significantly with decreasing film thickness.

To summarize this section, TA spectra of the 3D and 2D TI Bi$_2$Se$_3$ films measured with low-power IR pumping show characteristics that are similar to those reported for more powerful pumping. The high efficiency of two-photon excitation of Dirac fermions from the Dirac SS1 to the Dirac SS4 [Fig. 1(e)] is associated with the giant nonlinearity of 2D Dirac systems. This observation suggests that the two-photon pumping of Dirac fermions should be taken into account in pump-probe experiments even at low pumping powers applied.

### B. Pump-probe traces of 10 and 2 QL thick Bi$_2$Se$_3$ films.

The corresponding pump-probe traces represent the relaxation dynamics of carriers photoexcited by an IR pumping pulse and probed at a certain wavelength (photon energy). Figures 2, 3 and 4, 5 show the pump-probe traces of the 3D and 2D TI Bi$_2$Se$_3$ measured using the low-power and high-power pumping regimes, respectively. The traces were plotted as a function of probing photon energy and presented in different plots either together or separately using different delay-time scales for better observation.
In contrast, this type of \( s \)-\( ir \) is also confirmed by the fact that the fast and spatial not necessarily stage and the long excitation of coherent acoustic phonons a single is most likely transformed dynamics of relaxation dynamics. For \( \text{Bi}_2\text{Se}_3 \) nature of the response \([Figs. 2, 3 and 6(a), (b), (c)]\). In addition, the pump-probe traces contain the fast-decay and long-decay stages. However, the two fast-decay stages show different decay-time constants of \(~5.0\) and \(~1.2\) ps for probing photon energies ranging from \(~3.6\) to \(~2.5\) eV and from \(~2.0\) to \(~1.65\) eV, respectively. This behavior unambiguously indicates the presence of two different relaxation dynamics. Moreover, the fast-decay relaxation dynamics of the first spectral region smoothly transforms into the long-decay dynamics with a decay-time constant of \(~600\) ps. In contrast, the fast-decay relaxation dynamics arising in the second spectral region is most likely transformed first into the longer dynamics including a single-cycle oscillation, which is usually associated with the excitation of coherent acoustic phonons,\(^{10,12,15}\) and then into the long-decay dynamics \([Fig. 2, 3 and 6(c)]\). However, the fast-decay stage and the single-cycle oscillatory behavior in the latter case are not necessarily unique since both disappear upon probing at photon energies exceeding \(~2.0\) eV. Consequently, they refer rather to the spatial redistribution of electrons upon relaxation between Dirac SS and the bulk states than to the coherent acoustic phonons.\(^{23}\) This conclusion is also confirmed by the fact that the fast-decay stage at certain probing photon energies ranging from \(~2.0\) to \(~2.5\) eV is completely absent. The latter behavior means that the long-decay stage completely determines the dynamics of carrier relaxation in this probing region. In addition, the long-decay stage remains nearly unchanged within the entire probing region \([Fig. 6(c)]\). Thus, totally three relaxation dynamics can be distinguished, associated with the two fast-decay stages and a long-decay stage, which explicitly manifest themselves in different probing regions. The observed non-monotonic behavior of the AB signal with probing photon energy confirms a spatial redistribution of carriers upon relaxation. This spatio-temporal carrier dynamics is usually associated with the vertical electron transport.\(^{16,23}\)

Additionally, the rise-time constant of the pump-probe traces gradually shortens when probing at lower photon energies from its initial value of \(~0.25\) ps at \(~3.6\) eV to \(~0.1\) ps at \(~2.1\) eV, being stabilized afterward \([Figs. 2, 3 and 6(g)]\). The latter dynamics weakly depends on pumping power and is accompanied by a temporal shift in the onset of the pump-probe traces from their actual zero-time, thereby demonstrating an opposite tendency with decreasing probing photon energy \([Fig. 6(g)]\). Here we would like to especially emphasize that this type of correlation can be

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**FIG. 3.** Pump-probe traces of the 3D TI Bi$_2$Se$_3$ (10 QL thick film) measured at different probing wavelengths (photon energies), as indicated by the corresponding colors, using the \(~730\) nm pumping (\(~1.7\) eV photon energy) of \(~3.0\) mW average power (\(~27\) GW cm$^{-2}$ pulse peak intensity, \(~1.0\) mJ cm$^{-2}$ absorbed fluence). All plots show the same set of traces plotted together or separately using different delay-time scales.
observed only if IR pumping is applied. Alternatively, it was found that the pump-probe traces measured using one-photon UV pumping with a photon energy of ~3.65 eV show exclusively a temporal shift in their onset with decreasing probing photon energy, whereas the rise-time constant remains fixed. This behavior additionally confirms the existence of the two fast-decay relaxation dynamics in the IR pumped 3D TI Bi₂Se₃, one of which replaces the other when probing in different spectral regions.

We associate these two fast-decay relaxation dynamics with the vertical electron transport that balances the carrier populations of Dirac SS and the bulk states upon relaxation. On the contrary, the base amplitude of the AB signal and its long-decay stage characterize the overall relaxation tendency. To be more specific, we first consider two mechanisms that could potentially contribute to the AB response. One of them deals with the integrated phase-space filling with photoexcited electrons, which indirectly causes a change in the complex refractive index of the material in a wide spectral region. The word “integrated” is used to distinguish the filling of the phase-space in all possible states situated above the CB edge from the ordinary Burstein-Moss effect. The discussed mechanism is almost nonselective in the energy spectrum far from the bandgap and is very common for pump-probe reflectivity experiments that use the pumping and probing beams of the same wavelengths. This mechanism is mainly governed by electrons that were initially one-photon-excited from the VB (BS1) into the CB (BS2) [Fig. 1(e)]. Further relaxation of electrons through the Frohlich scattering mechanism is accompanied by their vertical transport to the Dirac SS2 and, consequently, a loss of electron mass. This process manifests itself in the pump-probe traces as the fast-decay stage when probing at photon energies ranging from ~3.6 to ~2.5 eV and exhibit a small amplitude (Figs. 2 and 3) with a decay time constant of ~5.0 ps [Fig. 6(b)]. The final relaxation stage of massless Dirac fermions residing in the Dirac SS2 is their recombination with holes residing in the Dirac SS1. The latter process is responsible for the long-decay stage with a decay-time constant of ~600 ps. The corresponding pump-probe traces originate at the actual zero-time and their amplitude increases with a rise-time constant of ~0.25 ps, which is a measure of electron-electron thermalization in the bulk states [Fig. 1(e)].

Alternatively, the effect of two-photon-excited Dirac fermions on the complex refractive index modulation in the bulk is negligible. This behavior is confirmed by the fact that the amplitude of the

FIG. 4. Pump-probe traces of the 2D TI Bi₂Se₃ (2 QL thick film) measured at different probing wavelengths (photon energies), as indicated by the corresponding colors, using the ~730 nm pumping (~1.7 eV photon energy) of ~0.5 mW average power (~4 GW cm⁻² pulse peak intensity, ~16 µJ cm⁻² absorbed fluence). All plots show the same set of traces plotted together or separately using different delay-time scales.
pump-probe traces in the probing photon energy range in nearby two-photon pumping is minimal. Consequently, the relaxation of two-photon-excited Dirac fermions manifests itself through the direct Pauli blocking mechanism.\[16,23\] This mechanism is selective to Dirac SS, which spatially extend from the surface into the bulk to a critical distance of ~3 nm (the half of the critical film thickness at which a gap opens in Dirac SS).\[32\] Because this mechanism is governed by the local density of Dirac fermions at a certain energy, the AB response becomes spectrally sensitive within the entire region of probing photon energies. However, this mechanism immediately switches to the integrated phase-space filling one when Dirac fermions gain masses upon reaching the non-topological bulk states in which the time-reversal symmetry is broken.\[33\] We note that the latter process is not associated with the opening of a gap in Dirac SS,\[12,34\] but rather is caused by Dirac fermion transfer to a distance exceeding the critical distance from the surface. For this reason, the surface-to-bulk vertical transport of Dirac fermions strongly depends on the film thickness and the density of photoexcited carriers and, therefore, can be observed exclusively for the 3D TI Bi$_2$Se$_3$ (10 nm thick film in our case). The discussed relaxation of nonequilibrium Dirac fermions depicts hence their transient accumulation in certain bulk and surface states situated at energies below the two-photon pumping energy (BS4, BS3, SS3, BS2 and SS2). Most importantly, massless Dirac fermions tend to occupy the bulk states during relaxation more and more due to the higher density of states and a much higher relaxation rate for the bulk states as compared to Dirac SS.\[23\] This behavior implies that the distance over which Dirac fermions move from the surface into the bulk gradually increases upon relaxation, thus ultimately leading to a change in the mechanism that determines the AB signal. The latter dynamics is illustrated by the amplitude of the AB response that steadily increases when probing at lower photon energies below the energy corresponding to two-photon pumping (Figs. 2 and 3). This behavior of pump-probe traces reflects the same dynamics that is manifested in the TA spectra [Fig. 1(e)]. The direct Pauli blocking mechanism is hence additional to the integrated phase-space filling mechanism and mainly manifest itself on a subpicosecond time scale. This behavior is also confirmed by a change in the electron relaxation rate, as discussed above [Fig. 1(g)]. Furthermore, the onset of the pump-probe traces shows a temporal shift from the actual zero-time, since it takes some time for the relaxing Dirac fermions to reach the lower energy states, which are directly probed. The corresponding rise-time constant (~0.1 ps) is governed rather by an initial temporal

FIG. 5. Pump-probe traces of the 2D TI Bi$_2$Se$_3$ (2 QL thick film) measured at different probing wavelengths (photon energies), as indicated by the corresponding colors, using the ~730 nm pumping (~1.7 eV photon energy) of ~3.0 mW average power (~27 GW cm$^{-2}$ pulse peak intensity, ~27 µJ cm$^{-2}$ absorbed fluence). All plots show the same set of traces plotted together or separately using different delay-time scales.
profile of photoexcited Dirac fermions than by their actual electron-electron thermalization. This behavior means that the electron-electron thermalization of Dirac fermions in Dirac SS is comparable to or shorter than the pumping pulse duration (~0.1 ps).

Once Dirac fermions accumulate in the BS2, where they gain masses and begin to contribute through the integrated phase-space filling mechanism, the AB response reaches its maximum amplitude and shows exclusively a long-decay contribution when probing in the range of ~2.0 – 2.5 eV. Further relaxation is associated with the bulk-to-surface vertical transport (from BS2 to SS2), which manifest itself as the second fast-decay stage, probed at photon energies ranging from ~2.0 to ~1.65 eV [Figs. 2, 3, (a)]. The effect of this fast-decay relaxation dynamics gradually increases when approaching energy corresponding to the Dirac SS2 in which Dirac fermions accumulate before recombination. The shorter decay-time constant of this fast-decay relaxation dynamics (~1.2 ps), as compared to the first fast-decay stage (~5.0 ps), indicates a more efficient vertical electron transport. This behavior also includes a single-cycle oscillation resulting from the spatial redistribution of electrons toward the Dirac SS2, followed by a recoil effect that partially move electrons back to the bulk states.23

We also note that the final relaxation dynamics of two-photon-excited Dirac fermions before recombination is their transient accumulation in the Dirac SS2, similarly to how it happens with the one-photon-excited electrons in the bulk. The accumulation of Dirac fermions in the Dirac SS2 has also been confirmed by higher nonequilibrium mobility of carriers found for these states, as compared to the equilibrium conductivity in the Dirac SS1.22

A remarkable feature of the 3D TI Bi2Se3 is the appearance of coherent LO-phonon oscillations in the pump-probe traces. These oscillations are manifested exclusively at the energies of the probing photons, where the fast-decay stages appear (Figs. 2 and 3). On the contrary, for the probing photon energy range of ~2.0 – 2.5 eV, in which the fast-decay stage and the corresponding vertical
electron transport are absent, the coherent LO-phonon oscillations do not manifest themselves. Furthermore, the coherent LO-phonon oscillations reveal the same frequency of ~2.2 THz and the damping time constant of ~2.1 ps for both probing regions [Fig. 6(a) and (b)], which are typical for the bulk states.\textsuperscript{7,10-13,23} The correlation between the appearance of the fast-decay stages and the coherent LO-phonon oscillations indicates that the cooling of hot carriers due to Fröhlich interaction (the successive launching of LO-phonons) is accompanied by the LO-phonon-assisted vertical electron transport.\textsuperscript{23} Furthermore, as pumping power increases, the vertical electron transport is enhanced, and the coherent LO-phonon oscillations become more pronounced. We consider the vertical transport of carriers during their relaxation as a mechanism that spatially synchronizes the electron-phonon scattering events in the bulk, thus introducing coherence into the system. Accordingly, the coherent LO-phonon oscillations appeared in pump-probe traces in the probing photon energy range of ~3.6 - 2.5 eV are associated with the LO-phonon-assisted surface-to-bulk vertical transport (from SS4 to BS4 and from SS3 to BS3 and BS2). In contrast, the coherent LO-phonon oscillations appeared in the range of ~2.0 - 1.65 eV can be attributed to the LO-phonon-assisted bulk-to-surface vertical transport (from BS2 to SS2).

For the 2D TI Bi$_2$Se$_3$, since a film thickness of ~2 nm is associated with the topologically trivial insulator phase,\textsuperscript{32,33} the observed relaxation dynamics is mainly governed by the two-photon-excited massive Dirac fermions.\textsuperscript{34} The spatial confinement of massive Dirac fermions also causes their high density and, consequently, the inverse bremsstrahlung type FCA in the Dirac SS2.\textsuperscript{23} As discussed above, this behavior leads to the appearance of both negative and positive contributions to the TA spectra [Fig. 1(a) and (b)]. The corresponding AB and FCA pump-probe traces (Figs. 4 and 5) shows that the characteristic energy of the probing photons, at which the pump-probe traces change sign, shifts towards higher energies with increasing pumping power. This behavior is another manifestation of the same dynamics that was discussed for the TA spectra. We also note that the AB and FCA pump-probe traces reveal much shorter decay-time constants as compared to the 3D TI Bi$_2$Se$_3$ [Fig. 6(a) - (f)]. This observation confirms the general tendency according to which the rate of electron-hole recombination increases with decreasing film thickness.\textsuperscript{14}

For the low-power pumping regime, the temporal shift in the onset of the AB pump-probe traces and the reduction in their rise-time constants with decreasing probing photon energy are very similar to those observed for the 3D TI Bi$_2$Se$_3$ [Fig. 6(g) and (h)]. However, as pumping power increases, the rise-time constant of the AB pump-probe traces becomes independent of probing photon energy, thereby demonstrating a similar trend observed for one-photon UV pumping.\textsuperscript{24} This behavior suggests that the influence of the AB mechanism associated with the integrated filling of the phase-space in the bulk states becomes negligible with increasing pumping power. Consequently, the relaxation dynamics of massive Dirac fermions in this case is mainly appeared through the direct Pauli blocking mechanism.

One of the most interesting dynamics, which manifest itself in the pump-probe traces of the 2D TI Bi$_2$Se$_3$, is associated with the overlap of positive and negative contributions. Since the positive contribution characterizes FCA in the Dirac SS2 and, therefore, arise exclusively when the two-photon-excited massive Dirac fermions transiently accumulate in these states, the onset of the FCA pump-probe traces shows a significant temporal shift from the actual zero-time. This behavior appears as a negative narrow feature in the AB pump-probe traces on a subpicosecond time scale [Fig. 6(e)], which is caused by the overlap of the negative and positive contributions. It is important to note that as soon as the FCA pump-probe traces appear at a certain photon energy, there is no noticeable temporal shift in their onset and no change in the rise-time constant with a further decrease in probing photon energy [Fig. 6 (i)]. This relaxation dynamics clearly indicates that the accumulation of massive Dirac fermions in the Dirac SS2 is the final relaxation stage before recombination.

The temporal overlap of the AB and FCA pump-probe traces also influences the appearance of coherent LO-phonon oscillations. The vertical transport of massive Dirac fermions in the 2D TI Bi$_2$Se$_3$ is significantly weakened. As a result, coherent LO-phonon oscillations appear exclusively in the FCA pump-probe traces [Figs. 4, 5, and 6(d), (e)]. However, because of the overlap of the positive and negative contributions, the AB pump-probe traces show coherent LO-phonon oscillations that replicate those associated with the FCA response. This tendency is confirmed by the lower frequency of coherent LO-phonon oscillations in Dirac SS (~2.05 THz),\textsuperscript{7,23} and the constant phase of oscillations for all traces observed at different energies of the probing photons. The launching of coherent LO-phonon oscillations in Dirac SS is likely governed by the in-phase successive quasi-elastic scattering of massive Dirac fermions from the uppermost atomic layer of the films. The in-phase launching in this case means that the sources of the Dirac fermion scattering are not spatially separated, as that occurs in the bulk states.

**Conclusions**

In summary, using UV-Vis TA spectroscopy, we have shown that in pump-probe experiments on the 2D and 3D TI Bi$_2$Se$_3$ exploiting IR pumping with a wavelength of ~730 nm (1.7 eV photon energy)], even at low-power pumping with absorbed fluences in the $\mu$J cm$^{-2}$ range, TA spectra cover the entire visible and part of the UV region. This observation unambiguously proves the two-photon pumping regime. We attributed the high efficiency of two-photon pumping to the giant nonlinearity of Dirac fermions in Dirac SS. Alternatively, one-photon pumping is associated with the excitation of bound valence electrons in the bulk into the conduction band. Two mechanisms of absorption bleaching have been identified, which we associate with direct Pauli blocking in Dirac SS and an integrated filling of the phase-space in the bulk states. We suggested that the coherent launching of LO-phonon oscillations in the bulk states and Dirac SS is due to the vertical electron transport and the in-phase sequential scattering of Dirac fermions from the uppermost atomic layer, respectively. Finally, we concluded that the two-photon IR pumped UV-Vis TA spectroscopy of Dirac fermions is a powerful and selective tool for studying ultrafast relaxation dynamics in 2D Dirac systems.

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