Ultrafast Photoconductivity and Terahertz Vibrational Dynamics in Double-Helix SnIP Nanowires

David N. Purschke,* Markus R. P. Pielmeier, Ebru Üzer, Claudia Ott, Charles Jensen, Annabelle Degg, Anna Vogel, Naaman Amer, Tom Nilges, and Frank A. Hegmann*

Tin iodide phosphide (SnIP), an inorganic double-helix material, is a quasi-1D van der Waals semiconductor that shows promise in photocatalysis and flexible electronics. However, the understanding of the fundamental photophysics and charge transport dynamics of this new material is limited. Here, time-resolved terahertz (THz) spectroscopy is used to probe the transient photoconductivity of SnIP nanowire films and measure the carrier mobility. With insight into the highly anisotropic electronic structure from quantum chemical calculations, an electron mobility as high as 280 cm$^2$ V$^{-1}$s$^{-1}$ along the double-helix axis and a hole mobility of 238 cm$^2$ V$^{-1}$s$^{-1}$ perpendicular to the double-helix axis are detected. Additionally, infrared-active (IR-active) THz vibrational modes are measured, which shows excellent agreement with first-principles calculations, and an ultrafast photoexcitation-induced charge redistribution is observed that reduces the amplitude of a twisting mode of the outer SnI helix on picosecond timescales. Finally, it is shown that the carrier lifetime and mobility are limited by a trap density greater than $10^{18}$ cm$^{-3}$. The results provide insight into the optical excitation and relaxation pathways of SnIP and demonstrate a remarkably high carrier mobility for such a soft and flexible material, suggesting that it could be ideally suited for flexible electronics applications.

1. Introduction

The importance of the double helix structure in biology has led to significant fundamental interest in abiotic and inorganic analogues.[1–5] Tin iodide phosphide (SnIP) recently surprised the inorganic materials community as the first carbonless atomic-scale double helix.[6] Subsequently, several compounds were predicted to form with the SnIP structure, indicating that SnIP could be the first of a new class of inorganic double-helix materials.[7–9] With strong intra-helix covalent bonds and weak inter-helix dispersion forces, SnIP belongs to the group of newly emerging 1D van der Waals (vdW) materials with potential applications in nanoelectronics and photonics.[10–13] In contrast to the DNA structure, which consists of two equal radius helices, SnIP forms with an outer [SnI]$^+$ helix wrapping around an inner [P]$^-$ helix, as pictured in Figure 1a. SnIP crystallizes monocrinally with a unit cell containing two opposite-handed double helices so that there is no net chirality. It is composed of abundant and non-toxic elements and can grow uninhibited to cm-length needles with a low-temperature synthesis[6,14] (Sections S1 and S2, Supporting Information) or in nanotubes using vapor deposition.[15,16] Its 1.86 eV band gap, as determined by band structure calculations (Figure 1b,c) and verified experimentally (see ref. [6] and Section S3, Supporting Information), is well situated for solar absorption and photocatalytic water splitting.[8,10,15] SnIP is also an extremely soft and flexible semiconductor and is therefore a promising material for applications in flexible electronics,[6,10] where these properties are highly desirable.[7] It is predicted to have a high carrier mobility,[8] however, as-grown SnIP is highly resistive so that the current lack of doped samples has made it difficult to explore its electronic properties.[6] Moreover, despite the exciting properties and unique structure of SnIP, there have been no investigations probing its ultrafast photophysical properties.

Here, we use time-resolved terahertz (THz) spectroscopy (TRTS) to study picosecond charge carrier dynamics in SnIP nanowire films, as shown in Figure 1d. TRTS, a powerful non-contact ultrafast probe, has been used extensively to probe carrier dynamics in low-dimensional materials, accelerating scientific understanding of transport mechanisms and enabling materials optimization for potential applications.[18,19] From analysis of the photoconductivity spectra, along with insight into the highly anisotropic energy landscape from density functional theory (DFT), we make the first measurement of the carrier mobility in SnIP. We find a maximum electron mobility of 280 cm$^2$ V$^{-1}$s$^{-1}$ along the double-helix axis, an extraordinarily high mobility for a material as soft and flexible as SnIP. On
the other hand, the hole mobility is largest perpendicular to the double-helix axis and is as high as 238 cm$^2$/V·s, which is comparable to the hole mobility in silicon or gallium arsenide.[20] Using terahertz time-domain spectroscopy (THz-TDS), we also make the first observation of IR-active vibrational modes in SnIP, finding two resonances in the THz range that we assign to rocking and twisting modes of the outer [SnI]$^+$ helix by comparison to quantum-chemical calculations. Interestingly, we see a suppression of the photoconductivity near a strong resonance at 1.495 THz, which indicates a reduction in oscillator strength after photoexcitation due to a photoexcitation-induced charge redistribution.[19,21–23] Tracking the time evolution of the oscillator parameters, we see that the charge redistribution occurs on a timescale comparable to the lifetime of the mode. Finally, we show that the carrier lifetime is limited by ultrafast trapping and estimate the trap density to be greater than 10$^{18}$ cm$^{-3}$. This suggests that the carrier lifetime and mobility could be improved by optimized synthesis or passivation of traps, which would dramatically enhance photocatalytic activity.[24,25] Most importantly, our results provide the first evidence of high carrier mobility in SnIP and show that it is, to our knowledge, more than an order of magnitude larger than that of any comparably soft and flexible material.

2. Results and Discussion

2.1. Terahertz Vibrational Modes

We measured the effective dielectric function, $\tilde{\varepsilon}_i = \varepsilon_i + i\varepsilon_i$, of the SnIP nanowire film using THz-TDS in the frequency range from 0.5 to 2.5 THz. As shown in Figure 1e, a weak vibrational resonance at 1.13 THz and stronger resonance at 1.495 THz are observed (referred to here as mode 1 and mode 2), and a high-frequency dielectric constant of $\varepsilon_\infty = 3.52$. The weighted average of the calculated imaginary dielectric constant assuming a 0.1 THz linewidth, $\varepsilon_2,\text{DFT}$, is plotted above. f,g) Calculated normal mode displacement vectors of the 1.52 THz oscillation projected along the $d$-axis (f) and $b$-axis (g).
on comparison to density functional theory (DFT) calculations using the Crystal software package.

While the random orientation of nanowires in our thin films obscures the underlying symmetry of the modes, making it more difficult to precisely assign peaks in the experimentally observed spectrum to individual modes, the calculated average imaginary dielectric function shows good agreement with data, as seen in Figure 1e. In general, the calculations suggest that motion in the 0.5–2.5 THz range is associated with oscillations of the [SnI]$^+$ (outer) helix. Two high intensity modes near mode 2 (1.495 THz) are revealed by DFT calculations at 1.52 and 1.55 THz. Both peaks can be classified as primarily twisting modes of the outer [SnI]$^+$ helix. Figure 1f, g shows the vibrational conformation of the 1.52 THz mode, the highest intensity mode in the 0.5–2.5 THz range. In this mode, the Sn$^{2+}$ and I$^-$ atoms show the largest displacement with motion predominantly along the double-helix axis so that the mode is longitudinally polarized with respect to the nanowires. A smaller peak near mode 1 (1.13 THz) is revealed by the calculated spectra at 1.15 THz, corresponding to rocking motion of the outer [SnI]$^+$ helix. For further discussion of the calculations, see Sections S4 and S5, Supporting Information, which includes plots of the polarization-dependent dielectric function and animations of several high intensity modes.

2.2. Transient Photoconductivity

To study the ultrafast carrier transport, we measure the carrier lifetime and photoconductivity for above-gap and below-gap excitation using TRTS, as shown schematically in Figure 2a. Briefly, a 400 or 800 nm photoexcitation laser pulse at a fixed time delay, $\Delta t_0$, with respect to the THz pulse modulates the THz transmission by generating free carriers in the SnIP film. The transmitted THz field is electro-optically sampled using a third optical pulse with time delay $\Delta t_2 = 0$ and monitored for changes induced by photoexcitation. In Figure 2b, we see the time-dependent pump-induced differential THz transmission, $-\Delta T/T_0$, with 400 and 800 nm pump wavelengths and 190 and 850 $\mu$J/cm$^2$ excitation fluences, respectively. The solid lines are biexponential fits with amplitudes $A_2 = 0.76 (0.54)$ and $A_1 = 0.24 (0.46)$, and lifetimes $\tau_2 = 2.6 (1.4)$ ps, and $\tau_1 = 20 (35)$ ps for 400 (800) nm excitation while the black dots are experimental data. The vertical dashed black lines indicate a time delay of 2.2 ps, which shows the THz-pulse waveform for 400 nm (top) and 800 nm (bottom) pump wavelengths at fluences of 190$\mu$J/cm$^2$ and 850$\mu$J/cm$^2$, respectively. The solid lines are biexponential fits with amplitudes $A_2 = 0.76 (0.54)$ and $A_1 = 0.24 (0.46)$, and lifetimes $\tau_2 = 2.6 (1.4)$ ps, and $\tau_1 = 20 (35)$ ps for 400 (800) nm excitation while the black dots are experimental data. The vertical dashed black lines indicate a time delay of 2.2 ps, which shows the THz-pulse waveform for 400 nm (top) and 800 nm (bottom) pump wavelengths. The solid lines are a fit to the model described in the text.

Figure 2. a) Schematic of the TRTS experiment. A THz pulse is coincident on a drop-cast SnIP thin film along with a time-delayed ($\Delta t_2$) 400 or 800 nm photoexcitation (pump) pulse. A third pulse is used as a gating beam at time delay $\Delta t_1$ for field-resolved electro-optic sampling of the transmitted THz pulse to monitor the pump-induced change in transmission. b) Pump-induced differential THz transmission as a function of pump-probe time delay with $\Delta t_2 = 0$ ps (indicated by the black arrow in the inset, which shows the THz-pulse waveform) for 400 nm (top) and 800 nm (bottom) pump wavelengths at fluences of 190$\mu$J/cm$^2$ and 850$\mu$J/cm$^2$, respectively. The solid lines are biexponential fits with amplitudes $A_2 = 0.76 (0.54)$ and $A_1 = 0.24 (0.46)$, and lifetimes $\tau_2 = 2.6 (1.4)$ ps, and $\tau_1 = 20 (35)$ ps for 400 (800) nm excitation while the black dots are experimental data. The vertical dashed black lines indicate a time delay of 2.2 ps, which shows the THz-pulse waveform for 400 nm (top) and 800 nm (bottom) pump wavelengths. The solid lines are a fit to the model described in the text.

The observation of photoconductivity with sub-gap excitation is interesting on its own, as it implies free carriers must be generated either by two-photon or band/defect-tail absorption. The linearity of 800 nm transmission (Section S8, Supporting Information) is inconsistent with two-photon absorption while the photon energy of 1.55 eV is too far below the 1.86 eV band gap for band-tail absorption, suggesting transitions from deep-level states are the dominant excitation channel (see Section S3, Supporting Information). The large amplitude of the signal, with similar photoconductivity at only 4.5 times the fluence (nine times the photon flux), is then somewhat surprising. This can be attributed in part to the increased thickness of the photoexcited layer due to the smaller absorption coefficient and partly to a high density of mid-gap states. It is also possible that weak light-trapping effects due to the nanowire-film morphology increase the effective interaction length of the 800 nm pulse.
The corresponding complex photoconductivity spectra for 400 and 800 nm excitation, acquired 2.2 ps after the peak of the transient photoconductivity, are shown in Figure 2c. Due to the geometry of the SnIP nanowires and needles, quantitative measurement of the optical penetration depth, \(d_0\), for a given excitation wavelength is difficult. As a result, we study the areal volume conductivity does not affect the measurement of carrier mobility, which is derived from the scattering time and is therefore a property of the dispersion rather than the amplitude of the conductivity. We can learn a great deal about the nature of photoconductivity by studying the qualitative properties of the spectra, which are quite similar for 400 and 800 nm despite the difference in excitation channels. There are two main features in the observed spectra. First, there is a broad increasing \(\Delta\sigma_1\) with frequency along with a corresponding negative \(\Delta\sigma_2\), which is characteristic of free-carrier localization. Second, there is a negative peak in \(\Delta\sigma_1\) with a corresponding kink in \(\Delta\sigma_2\) near mode 2, which indicates a photoexcitation-induced modification of the vibrational mode. To model the spectra, we treat these two contributions individually and use a fit function given by \(\Delta\sigma = \Delta\sigma_{DS} + \Delta\sigma_{PS}\), where \(\Delta\sigma_{DS}\) is the Drude–Smith model of optical conductivity and \(\Delta\sigma_{PS}\) is the peak-shift model of the differential conductivity of a Lorentz oscillator. The solid lines in Figure 2c show a simultaneous fit to the real and imaginary conductivity using this model, with fit parameters summarized in Table 1. In the following two sections we discuss each of these contributions in detail.

### 2.3. Free-Carrier Response and Anisotropic Carrier Mobility

Several models are commonly applied to understand broad features in the photoconductivity spectra, which are all used to describe a free-carrier (i.e., conductive) response. We note that the temperature dependence of the THz conductivity is consistent with band-like transport (see Section S10, Supporting Information). In Section S11, Supporting Information, we provide a detailed analysis of our data in terms of several different models (Bruggeman, Drude–Smith, and plasmon) and here summarize only the key criteria necessary to validate our eventual choice of the Drude–Smith model. Notably, the mobilities extracted from each model are similar, ranging from 150 to 280 cm²/V·s (Section S11, Supporting Information). Bruggeman effective-medium theory has been used to describe the conductivity in inhomogeneous systems; however, we could only achieve reasonable fit quality to our data with this model by introducing an unphysical scaling of the fill fraction with fluence. A Drude–Lorentz model has been used to describe surface plasmon resonances in nanowires or to describe a mixed Drude response along with hydrogen-like transitions in excitonic systems. While the plasmon model provides excellent fit quality, it predicts a specific scaling of the resonant frequency with increasing excitation density, which we do not observe in our data. Moreover, in SnIP, there are no excitonic signatures in either the absorbance or photoluminescence spectra.

Alternatively, modified forms of Drude conductivity, such as the Drude–Smith model, are often applied to describe nanomaterial conductivity when carrier localization arises from nanoscale morphology. The Drude–Smith model has been shown to fit photoconductivity spectra over a broad frequency range; yield comparable conductivity to standard transport measurements; and provide qualitative information about carrier localization. The functional form is given by,

\[
\tilde{\sigma}_{DS}(\omega) = \frac{N e^2 \tau_{DS}/m}{1 - i\omega\tau_{DS}} \left(1 + \frac{\epsilon}{1 - i\omega\tau_{DS}}\right)
\]

where \(m\) is the effective mass, \(\tau_{DS}\) is the scattering time, \(\epsilon\) is the elementary charge, \(\epsilon\) is a phenomenological localization parameter that ranges from 0 to –1 for free and localized carriers, respectively, and \(N\) is the density of electron–hole pairs. Due to the uncertainty in penetration depth discussed previously, we fit with the areal charge density, \(d_0N\). For the mass we use the weighted average of the direction-dependent effective mass, \(m = \overline{m} = 0.24\), because our thin films consist of an ensemble of randomly-oriented nanowires (see Section S12, Supporting Information). It is clear that to quantitatively interpret the spectra, we must understand the effective mass anisotropy in SnIP, which we obtain from quantum-chemical calculations.

We can visualize the electronic structure by plotting the constant energy surfaces for the conduction (green) and valence (red) bands with a 5 meV offset from the extrema, as shown in Figure 3a. We can see that the band gap is indirect with the valence band maximum centered at the \(\Gamma\) point and two conduction band minima slightly offset from the \(Y\) point in the direction of the valence band (see Figure 1b,c for the full Brillouin zone and bandstructure as well as Section S13, Supporting Information). To extract the effective mass, the band structure was calculated on a uniform grid around the conduction and valence band extrema and the effective mass tensor was calculated from the inverse Hessian matrix (see Section S12, Supporting Information).

Due to the low symmetry of the crystal and anisotropy of bonding, with strong covalent interactions parallel to the double

| \(\lambda_{\text{pump}} [\text{nm}]\) | \(d_0 \cdot N [\text{cm}^{-2}]\) | \(\tau_{DS} [\text{fs}]\) | \(\epsilon\) | \(\Delta\lambda_{\text{exc}} [\text{THz} \cdot \mu\text{m}]\) | \(d_0 \cdot \Delta\omega_{\text{calc}} [\text{THz} \cdot \mu\text{m}]\) | \(d_0 \cdot \Delta\omega/2\pi [\text{THz} \cdot \mu\text{m}]\) |
|----------------|----------------|-------------|---|---------------------|---------------------|---------------------|
| 400            | 3.5 \times 10^{11} | 45          | –0.84 | –6.4                | 0.9 \times 10^{-3} | –9.1 \times 10^{-3} |
| 800            | 3.8 \times 10^{12} | 42          | –0.84 | –6.4                | 1.6 \times 10^{-3} | –6.2 \times 10^{-3} |

\(\Delta\omega_{\text{exc}}, \Delta\omega_{\text{ps}}, \) and \(\Delta\omega_{\text{calc}}\) are the photoexcitation-induced changes in oscillator resonant frequency, damping, and amplitude, respectively (see Section S16, Supporting Information). \(d_0\) is the photoexcited film thickness, so that \(d_0 \cdot N\) is the areal charge density.
helices (̂x direction) and weak vdW interactions perpendicular to the double helix ( ̂y and ̂z directions), we expect anisotropy in the ̂x-direction effective mass in comparison to the ̂y and ̂z directions. This intuition holds for the conduction band, where \( m_{\text{eff}} = 0.28 \), where \( m_0 \) is the free-space electron mass, is the preferred transport direction, while the ̂y and ̂z masses are both significantly heavier. Here, we use the notation ̂x and ̂z because the principle axes of the effective mass tensor in the xz-plane (b) and yz-plane (c) with the vectors of the principle axes of the effective mass tensor for the conduction band (green) and valence band (red) shown in the bottom right corners. The directions of the colored vectors in (b), which are rotated with respect to the Cartesian axes ( ̂x, ̂y, ̂z), define the directions of ̂x and ̂z for the conduction band (green) and valence band (red). The preferred transport directions (directions of highest mobility) are indicated by the dashed green arrow for the conduction band (labeled \( \mu_{\text{c,\text{max}}} \)), which is almost parallel to the double-helix axis, and the dashed red arrow for the valence band (labeled \( \mu_{\text{v,\text{max}}} \)), which is almost perpendicular to the double-helix axis in the ̂z direction. Additionally, the helicity of adjacent planes of double helices is indicated schematically.

The calculation also reveals large anisotropy in the effective masses in the plane perpendicular to the double-helix axis as \( m_{\perp} < m_{\parallel} \) for both the conduction band and valence band. This anisotropy is more surprising, however, we highlight an additional asymmetry in the ̂y and ̂z directions that affects the interhelix interaction strength. As seen in Figure 3b,c, which shows projections of the crystal structure onto the xz and yz planes, stacking in the ̂z direction consists of alternating planes of right and left handed helices. Conversely, in the ̂y direction, the stacking planes themselves are composed of alternating left and right handed helices with a buckled structure. This asymmetry, which results in anisotropic van der Waals interactions, has also been shown to directly affect the anisotropic mechanical properties of SnIP.[10]

With knowledge of the effective mass, from the Drude–Smith portion of the fits in Figure 2c we can now extract the areal charge density, localization parameter, and scattering time. Good fits were obtained for three different fluences ranging from 40 to 470 \( \mu \text{J cm}^{-2} \) with a scattering time that decreases with fluence and a similar localization parameter, indicating that the Drude–Smith model effectively describes the photoconductivity spectra over an order of magnitude range of fluences (see Section S11, Supporting Information). The measured localization parameter of \( \sim 0.82 \), which is a similar to that observed in 1D systems such as graphene nanoribbons and carbon nanotubes, indicates that carriers are highly localized.[43] We note that implicit in our model is the approximation that the Drude–Smith scattering time, measured to be \( \tau_{DS} = 45 \text{ and 42 fs for 400 and 800 nm excitation, respectively, is isotropic and the same for electrons and holes. In combination with the calculated effective mass, the measured scattering time allows us to extract the carrier mobility. In the Drude–Smith model (Equation (2)), the mobility is given by \( \mu = \frac{e\tau_{DS}}{m} \) and we can study the anisotropic carrier mobility by using the direction-dependent mass instead of \( m \) as in the Drude–Smith fits.

Along the ̂x direction (almost parallel to the double-helix axis, dashed green arrow in Figure 3b), with \( m_{\perp} = 0.28 \), we find an electron mobility of 280 cm\(^2\) V\(^{-1}\) s\(^{-1}\) while along the ̂y direction, with \( m_{\parallel} = 2.0 \), we find a much smaller carrier mobility of 39 cm\(^2\) V\(^{-1}\) s\(^{-1}\) indicating a significant anisotropy in the carrier mobility (see Section S12, Supporting Information, for a complete summary of the anisotropic mobility). Alternatively, the hole mobility is largest in the ̂z direction (almost perpendicular to the double-helix axis, dashed red arrow in Figure 3b), and with \( m_{\perp} = 0.33 \) we find a hole mobility of 238 cm\(^2\) V\(^{-1}\) s\(^{-1}\). Such a high mobility is similar to other vdW materials[12,51] and many times higher than mobilities in organic semiconductors with comparable mechanical properties often used in flexible electronics.[52] The carrier mobility in these ultrathin materials is strongly affected by both static and dynamic disorder, which can strongly perturb orbital overlap and inhibit transport.[50,53] In a survey of a wide variety of materials, we find the combination of high mobility and low bulk modulus seen in SnIP is quite rare and rivaled only by several soft, high-mobility, perovskites. Furthermore, these materials are known to be quite fragile and, in this regard, the extreme flexibility displayed by SnIP makes it unique. Alternatively, of the comparatively soft and flexible materials we found, the polymers i-TPU and

![Figure 3](image-url)
PEDOT:PSS show the highest mobilities, which are still less than 20 cm² V⁻¹ s⁻¹, that is, more than 10 times lower than that of SnIP (see Section S14, Supporting Information).

From the large negative $c$ parameter, we can also see that long-range conductivity is reduced by localization due to the nanoscale morphology. This can be seen quantitatively with the long-range mobility, $\mu_{LR} = \mu(1 + c)$, which is equal to $\mu_{LR} = 45$ cm² V⁻¹ s⁻¹ in the $x$ direction. A detailed analysis (see Section S7, Supporting Information) indicates that the characteristic length scale defining long-range transport in our samples is on the order of 20 nm, which is several times smaller than the average nanowire diameter and indicates that, for example, grain boundaries within nanowires are the origin of localization.[44,48] This highlights an advantage of THz spectroscopy, where the high frequency field naturally probes transport on small length scales, as discussed in Section S7, Supporting Information, and can therefore give an indication of the intrinsic mobility in nanostructured materials. Future work will focus on optimizing material synthesis and processing to mitigate the effects of localization and improve the long-range mobility.

2.4. Peak-Shift and Picosecond Charge Redistribution Dynamics

We now shift focus to the narrow feature in the spectrum near 1.5 THz. The fingerprints of low-frequency vibrational dynamics on TRTS spectra has been the focus of several recent studies that have elaborated on a variety of interesting mechanisms.[21–23,47,54–60]. Narrow features in the conductivity spectrum are often attributed to resonant modulation of the conductivity due to polaronic effects from polaron longitudinal-optical (LO) modes.[47,58,59] However, here we estimate the LO mode to be at a significantly higher frequency of 1.73 THz (see Section S15, Supporting Information). The close proximity of the feature in the photoconductivity spectra to the transverse-optical (TO) mode at 1.495 THz, which does not couple strongly through the polar-optical mechanism responsible for strong electron–phonon coupling,[61] instead suggests that the lineshape of mode 2 is modified by photoexcitation on a picosecond timescale.[21–23,57] To fit this part of the spectra, we therefore use the peak-shift model of Zhao et al.,[23] which allows us to quantify the change in amplitude, $\Delta\sigma_{\text{osc,2}}$, resonant frequency, $\Delta\omega_{\text{2}}$, and damping, $\gamma_{\text{2}}$, of mode 2. For a detailed discussion of this model, see Section S16, Supporting Information. As discussed previously, we do not know the exact photoexcited film thickness, $d_0$, which we address by using $d_0\Delta\sigma_{\Delta\sigma}$ and using $d_0\Delta\omega_{\Delta\omega}$ and $d_0\gamma_{\Delta\gamma}$ as fit parameters.

The peak-shift portion of the fitting indicates a large photoexcitation-induced reduction in the amplitude along with a small reduction in linewidth and blue shift of the resonant frequency (for an estimation of the absolute change in lineshape, see Section S16, Supporting Information). This behavior indicates that screening from the photoexcited carriers induces a charge redistribution that stiffens the potential-energy landscape of this mode and reduces its effective charge, that is, reduces its dipole moment.[19,21–23] Interestingly, when the screening length is large compared to the interatomic spacing, as is the case in this work (see Section S17, Supporting Information), such modulation of IR-active modes is not expected in prototypical covalent semiconductors.[54,62,63] However, in more complex systems changes to the vibrational spectrum have been linked to a photoinduced charge redistribution at the atomic scale.[39,21–23,55]

This effect could be especially strong in SnIP due to the prevalence of long-range dispersion forces, which can be sensitive to free-carrier screening.[64] In addition to the amplitude reduction, from the fits we also see that the differential linewidth is negative, indicating a line narrowing. We speculate on two possible origins of this effect. First, the charge redistribution could lead to a lattice reorganization that reduces strain inhomogeneity,[55,66] which would result in less inhomogeneous broadening.[67] Second, it could result from a reduction of lattice anharmonicity, which is sensitive to dispersion forces[68] that can in turn be modified by screening.[64]

We can also study the time dependence of the conductivity after photoexcitation using a 2D scan, which allows us to probe the picosecond evolution of the charge redistribution. In Figure 4a,b we study the time evolution of the real and imaginary parts of the complex conductivity, respectively. The behavior of the vibrational mode is most striking in $\Delta\sigma_{\text{LR}}$, suggesting some sort of transient behavior in the differential oscillator parameters at early times. It is, however, important to identify and rule out early-time artifacts that arise due to the system response.[69,70] Our calculations (not shown) suggest that for the low amplitude of modulation observed here the extracted conductivity accurately represents the material conductivity for delay times larger than 0.5 ps after the peak of the transient photocconductivity (chosen as $\Delta t = 0$ ps), which itself is delayed from the arrival of the excitation pulse by approximately the system response (see Figure 4a,b).

Shown in Figure 4c are the time-dependent Drude–Smith fit parameters extracted from fitting the 2D conductivity to the model described in the previous section. The scattering time and localization parameter are stable throughout the entire window, which means the mobility is essentially constant over this range of time delays. In contrast, the peak-shift fit parameters, as seen in Figure 4d, show more interesting behavior. The change in resonant frequency, $\Delta\omega/2\pi$, shows evidence of oscillatory behavior as a function of time after excitation and the amplitude of negative differential amplitude and linewidth continue to grow until approximately 1 ps. We note the similarity between this 1 ps timescale and the oscillator lifetime, $\gamma^2 = 1$ ps. We can also see that the differential linewidth, which approaches zero by 3 ps, shows a faster recovery than the reduction in amplitude, which decays on a timescale similar to the extrapolated DC limit of the Drude–Smith fit function in equation 2, $\sigma_{\text{DC}}$, which is proportional to the carrier density. Finally, using the extracted fit parameters, we can decouple the Drude–Smith and peak-shift portions of the differential signal to visualize the time evolution of each separately, as seen in Figures 4e and 4f, respectively.

2.5. Trap Filling Dynamics and Defect Density

From the 2D scan in Figure 4 we also see that the differential transmission, $\Delta T$, and extrapolated DC conductivity, $\sigma_{\text{DC}}$, have very similar time dependence so that we can monitor
the relaxation of photoconductivity with a 1D scan along $\Delta t$.

**Figure 5a,b** shows the fluence-dependent normalized differential transmission with 400 and 800 nm excitation, respectively, revealing an increasing lifetime with fluence in both cases (see Section S18, Supporting Information, for the corresponding biexponential fit parameters). This response is characteristic of trap-filling dynamics.[24,71] Even at the highest fluence, the lifetime is still quite short, which implies that the surface states are non-saturable. We therefore propose that at low fluence ultrafast trapping in the bulk dominates relaxation, while at high fluence bulk traps are saturated and the lifetime is limited by surface recombination velocity.

We also study how the peak photoconductivity changes as a function of pump fluence, as seen in Figure 5c,d for 400 and 800 nm excitation, respectively. Here we see dramatically different behavior for 800 versus 400 nm excitation: the peak differential transmission increases sublinearly with 400 nm and superlinearly with 800 nm excitation. As we have already argued that two-photon absorption is not the dominant excitation channel for 800 nm excitation (see Section S8, Supporting Information), we instead attribute the super-linear behavior at low fluence to trapping on timescales faster than the system response time,[72] which is approximately 0.4 ps.

To fit the curve in Figure 5d, we use a rate equation model with one saturable and one non-saturable relaxation pathway combined with a Gaussian system response function (see Section S19, Supporting Information), which gives excellent quantitative agreement with data. From the $x$-intercept extrapolated linearly from the high fluence data (dashed line in Figure 5d) we find a saturation fluence of 150 $\mu$J cm$^{-2}$ (photon flux of $6 \times 10^{14}$ cm$^{-2}$), with which we can estimate the bulk trap density to be $6 \times 10^{18}$ cm$^{-3}$ by assuming a penetration depth of 1 $\mu$m (similar to the film thickness). Furthermore, an estimate based on the fluence-dependent lifetime with 400 nm excitation yields a similar trap density. Such a high trap density is also a likely source of scattering centers, which suggests that eliminating bulk defects by chemical passivation, optimized synthesis, or annealing would result in a significant enhancement in the carrier mobility. We note that some of the traps appear to be thermally activated, as the lifetime appears to increase with temperature (see Section S10, Supporting Information). Future studies exploring this behavior in more detail could provide more insight into the nature of these states.

To understand the saturation behavior with 400 nm excitation, we can rule out the introduction of new recombination channels as the lifetime does not decrease with increasing fluence.[72] We can also rule out optical nonlinearities (see Section S8, Supporting Information) and reduction of mobility at high fluence (see Section S11, Supporting Information). At high fluences the carrier density is greater than $10^{18}$ cm$^{-3}$ (see Section S11, Supporting Information), which is high enough that the quasi-Fermi level is pushed into the conduction band where the dispersion is highly non-parabolic. The electronic dispersion in these higher lying states becomes essentially flat in the

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**Figure 4.** a) Real part and b) imaginary part of the time evolution of the photoconductivity for 400 nm excitation at a fluence of 190 $\mu$J cm$^{-2}$. The inward facing ticks indicate time delays of $-0.4$ ps (the system response time) and $0.5$ ps (estimated time where transient artifacts no longer affect the signal). c) Time-dependence of the Drude–Smith fit parameters: the scattering time $\tau_{DS}$ (top), localization parameter $c$ (middle), and low frequency limit of the Drude–Smith fit, $\alpha_{DC} \cdot d$ with the time-domain differential transmission superimposed (bottom). d) Time-dependence of the differential oscillator parameters of mode 2 extracted from fits to the peak-shift model: the center frequency (top), linewidth (middle), and amplitudes (bottom), as a function of time delay. The shaded areas for time-delays less than $0.5$ ps indicate the region where early-time transient artifacts could potentially distort the extracted spectra. e,f) Evolution of the real part of the Drude–Smith (e) and differential oscillator (f) conductivity.
γ-direction and the system becomes effectively 2D in a large range of the Brillouin zone (see Section S13, Supporting Information). The sub-linearity at high fluence could therefore result from a combination of non-parabolicity in the \( \hat{x} \) and \( \hat{z} \) directions and a partial freeze out of transport in the \( \hat{y} \)-direction.

2.6. Ultrafast Excitation and Relaxation Pathways

Using the results described in the previous sections, we can develop a qualitative picture of excitation and relaxation channels in SnIP, as illustrated in Figure 6. The system consists of free states, corresponding to the delocalized conduction and valence bands, and trap states, which includes band-tail states and deep levels. With 400 nm excitation (above gap), electron–hole pairs are excited in band-like regions with a high joint density of states. Alternatively, with 800 nm excitation (sub gap), electrons are excited to or from regions with a high density of states in the gap to create free holes or electrons, respectively.

With 400 nm excitation (blue line in Figure 6a), carriers are generated with significant average excess energy, which must be dissipated before trapping, leading to a slower initial decay, \( \tau_f \), than with 800 nm excitation. This relaxation can involve both intraband and interband relaxation through multiple conduction/valence bands (indicated by \( C_i/V_i \) in Figure 6). Alternatively, with 800 nm excitation (red line in Figure 6a) carriers are generated with less excess energy and they can be trapped on timescales faster than the response time of the system, leading to the superlinear behavior seen in at low fluence Figure 5d. Notably, trapping on such fast timescales must occur via bulk trap states, as there is insufficient time for diffusion to the surface.

Finally, in Figure 6b,c, we illustrate the trap filling-behavior that leads to the lifetime enhancement observed at high fluence. With low fluence excitation (Figure 6b), the quasi-Fermi levels of electrons and holes are still within the gap and a high density of unoccupied traps is present. Alternatively, with high fluence excitation (Figure 6c), the quasi-Fermi levels have reached the band-like states and all traps are filled, resulting in an enhanced lifetime. This description applies to bulk traps, while the surface trap density is likely high enough to pin the quasi-Fermi levels to the middle of the gap even at the highest fluences. This distinction is especially important for applications in photocatalysis\(^{[10]}\) as it implies that a large fraction of carriers are trapped in the bulk before they can diffuse to active area at the surface. Our results therefore suggest that, in addition to an enhanced carrier mobility, eliminating bulk defects could lead to longer carrier lifetimes and therefore a significant enhancement in photocatalytic activity.\(^{[24,25,73]}\)

3. Conclusion

We have performed the first ultrafast spectroscopy and made the first measurement of carrier mobility of SnIP, a fundamentally exciting new inorganic double-helix material with extreme flexibility and quasi-1D nature. THz spectroscopy, supplemented by quantum-chemical calculations that reveal a highly anisotropic electronic structure, indicates that SnIP has a carrier mobility as high as 280 cm\(^2\) V\(^{-1}\) s\(^{-1}\), which is remarkably high...
Figure 6. a) Right: Schematic illustration of the DOS (black curve) with contributing conduction (green/blue) and valence (red/orange) bands. The DOS below/above the conduction/valence bands consist of traps due to band-tail states and deep-level defects. Left: Illustration of the excitation pathways for 400 nm (blue) and 800 nm (red) pump wavelengths. The 400 nm pump produces electron–hole pairs with significant excess energy while the 800 nm pump, which has sub-gap photon energy, excites either holes or electrons out of mid-gap trap states. b,c) Illustrations of the occupancy of electrons (green) and holes (purple) in the low-fluence (b) and high-fluences (c) cases. On picosecond timescales, the distribution can be approximated as thermal with a quasi-Fermi level for electrons and holes. In the low-fluence case, trap states near the band edge are not filled and carriers are rapidly trapped. Alternatively, in the high-fluence case, traps are filled and the lifetime is enhanced. The distribution of trap states can consist of band-tail states (exponential tails below/above the dotted line in the conduction/valence band DOS) and localized defect and impurity states within the gap (peaks near the middle of the gap).

4. Experimental Section

SnIP Synthesis and Thin Film Preparation: SnIP was grown by heating and annealing a stoichiometric mixture of SnI₄, Sn, and P₄O₁₀ in a vacuum-sealed argon-purged ampoule. The sample was cleaned in toluene to remove any unreacted SnI₄ and ultrasonicated to produce a suspension with a distribution of nanowires with, on average, 190 nm in diameter and 0.5-10 μm in length (Section S2, Supporting Information). The suspended SnIP was drop cast on a z-cut quartz wafer to produce an approximately uniform sample of 1.5 μm thickness suitable for THz spectroscopy (Figure 1d and Section S1, Supporting Information). Raman microscopy of a variety of ultrasonicated nanowires as well as powder X-ray diffraction (XRD) show only a small line-broadening on average compared to bulk SnIP needles, indicating the crystalline nature of the SnIP nanowires (Sections S20 and S21, Supporting Information). In addition to SnIP, the XRD reveals that the thin film contains a small amount of the clathrate compound Sn₂₄P₁₉.₃I₈.

Acknowledgements

The authors wish to acknowledge funding from the Natural Sciences and Engineering Research Council of Canada (NSERC Discovery Grant Program, NSERC CREATE-463990-2015), Deutsche Forschungsgemeinschaft (DFG Grant No. Ni 1095/8-1 and DFG IRTG 2022 for the Alberta/Technical University of Munich International Graduate School for Hybrid Functional Materials (ATUMS)), the Canada Foundation for Innovation (CFI), the Alberta Innovates Technology Futures (AITF) Strategic Chairs Program, and the e-conversion cluster via Germany’s Excellence Strategy - EXC 2089/1-390776260. They
also wish to acknowledge D. G. Cooke and T. L. Cocker for helpful discussions, A. Zeidler, F. Eckmann, and M. Stutzmann for use of their photothermal deflection spectroscopy system and valuable discussions, B. Shi, G. Popowich, and J. Chaulk for technical support, and S. Xu and the University of Alberta NanoFAB for the helium ion microscope measurements.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
double-helix nanowires, inorganic semiconductors, photoconductivity, photophysics, terahertz vibrational dynamics, ultrafast processes, van der Waals materials

Received: February 4, 2021
Revised: April 30, 2021
Published online: July 19, 2021

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