

Influence of excitation energy on microscopic quantum pathways for ultrafast charge transfer in van der Waals heterostructures

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Efficient charge separation in van der Waals (vdW) heterostructures is crucial for optimizing light harvesting and detection applications. However, precise control over the microscopic pathways governing ultrafast charge transfer remains an open challenge. These pathways are intrinsically linked to charge transfer states with strongly delocalized wave functions that appear at various momenta in the Brillouin zone. Here, we use time- and angle-resolved photoemission spectroscopy to investigate the possibility of steering carriers through specific charge transfer states in a prototypical WS₂-graphene heterostructure. By selectively exciting electron-hole pairs at the K point (A-exciton resonance) and close to the Q point (C-exciton resonance) of WS₂ with different pump photon energies, we find that charge separation is faster at higher excitation energies. This behavior is attributed to the fact that absorption at the C-exciton resonance generates electron-hole populations at energies well above the direct band gap. The resulting elevated carrier temperatures open an additional, highly efficient charge-transfer channel for holes in the WS₂ valence band, leading to an overall acceleration of interlayer hole transfer for C-exciton excitation. The microscopic insights gained in this work can be leveraged to optimize the performance of vdW heterostructures in optoelectronic devices.

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I. INTRODUCTION

The vast selection of two-dimensional (2D) materials available today, such as graphene and monolayer transition metal dichalcogenides, enables the design of novel heterostructures with tailored properties [1–3]. Such heterostructures commonly feature efficient absorption of visible light followed by ultrafast charge separation [4–10] with great potential for applications in light harvesting and detection. The driving force behind ultrafast charge separation is the band alignment, where photoexcited electrons and holes rapidly relax to the conduction band minimum and valence band maximum in separate layers. Charge transfer states, formed by hybridization between the vdW-coupled layers, create delocalized wave functions that serve as ultrafast tunneling channels [11–13]. These states occur at various momenta and energies in the Brillouin zone but do not contribute equally to charge separation. Based on existing models [11,13–18], the efficiency of different tunneling channels depends on the strength of the hybridization, the size of the energy barriers that photoexcited carriers must overcome to reach the charge transfer state, as well as the available tunneling phase space. The possibility to

steer carriers through specific charge transfer states, e.g., by selectively generating them at particular momenta and with controlled excess energies, remains unexplored.

Here, we investigate this concept in a prototypical vdW heterostructure consisting of monolayer WS₂ and graphene. We photoexcite the heterostructure with pump photon energies of $\hbar\omega = 2.0$ eV and $\hbar\omega = 3.1$ eV to excite electron-hole pairs at the K point (A exciton) and between the Γ and Q points (C exciton) of WS₂, respectively, and probe the charge transfer dynamics directly in the band structure using time- and angle-resolved photoemission spectroscopy (trARPES) [19]. We find that charge separation is significantly faster following $\hbar\omega = 3.1$ eV excitation, which we attribute to the activation of a second, highly efficient charge transfer channel in the valence band. Our findings introduce new possibilities for optimizing charge separation in vdW heterostructures, paving the way for more efficient light-harvesting and detection technologies.

II. METHODS

Sample growth. Pretreated 4H-SiC substrates were H etched to remove scratches and graphitized in Ar atmosphere. The resulting carbon monolayer with $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ structure was decoupled from the SiC substrate by H intercalation, yielding quasifreestanding monolayer graphene [20]. WS₂ was then grown by chemical vapour deposition from solid WO₃ and S precursors [21,22]. Both graphene and WS₂ growth were monitored using Raman spectroscopy, atomic force microscopy, and secondary electron microscopy. WS₂

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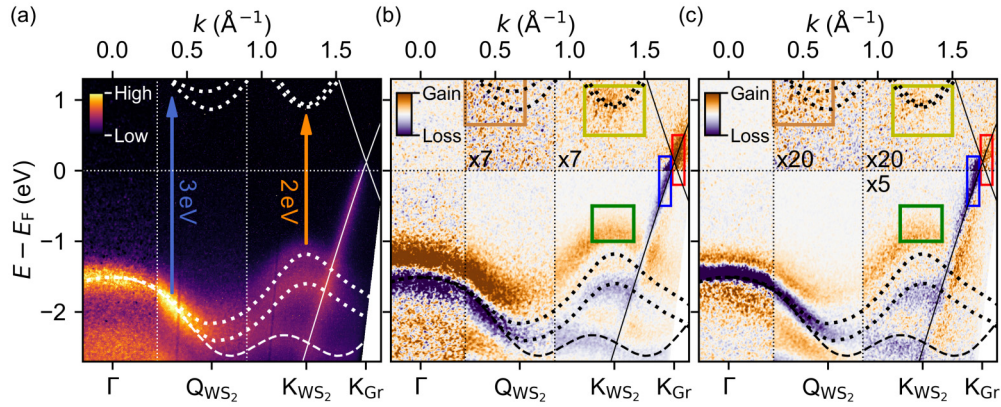


FIG. 1. trARPES data of WS₂-graphene heterostructure. (a) ARPES snapshots for negative pump-probe delay taken along the Γ K direction of graphene. Orange and blue arrows indicate the two different excitation schemes for $\hbar\omega = 2.0$ eV and $\hbar\omega = 3.1$ eV, respectively. Dotted, dashed, and continuous lines represent the theoretical band structures for WS₂ with twist angles of 0° and 30° [23] and graphene [24], respectively. (b) Pump-induced changes of the photocurrent in panel (a), 240 fs after excitation with $\hbar\omega = 2.0$ eV. (c) Same as panel (b) but 310 fs after excitation with $\hbar\omega = 3.1$ eV. Colored boxes in panels (b) and (c) mark the regions of integration for the pump-probe traces displayed in Fig. 2.

was found to grow in the shape of triangular islands with side lengths in the range of 300–700 nm with twist angles of either 0° or 30° with respect to the graphene layer [13].

trARPES. The setup was based on a Ti:Sa amplifier (Astrella, Coherent) with 1 kHz repetition rate, 35 fs pulse duration, 1.55 eV photon energy, and 7 mJ output power. Of this, 2 mJ were frequency doubled and used to drive high-harmonic generation in an Argon gas jet. The seventh harmonic at 21.7 eV was isolated using a grating monochromator and focused onto the sample with a beam diameter of 250 μ m. A small part of the 2 mJ output was frequency doubled to generate pump pulses with a photon energy of 3.1 eV with a fluence of 0.4 mJ/cm² at the focus. The remaining 5 mJ seeded an optical parametric amplifier (Topas Twins, Light Conversion). One of the signal beams was frequency doubled to generate pump pulses with a photon energy of 2.0 eV with a fluence of 1.7 mJ/cm² at the focus. The photoemitted electrons were detected with a hemispherical analyzer (Phoibos 100, SPECS) to obtain snapshots of the occupied band structure along the Γ K direction of graphene. The temporal and energy resolutions were ~ 200 meV and ~ 160 fs, respectively.

III. RESULTS

Figure 1(a) shows an ARPES image of the WS₂-graphene heterostructure at negative pump-probe delay before the arrival of the pump pulse. The dotted, dashed, and continuous lines indicate the theoretical band structures of WS₂ islands with a twist angle of 0° , WS₂ islands with a twist angle of 30° [23] and graphene [24], respectively. The bands are shifted in energy to fit the experimentally observed band alignment and doping level. Orange and blue arrows mark the electronic transitions in WS₂ excited at $\hbar\omega = 2.0$ eV and $\hbar\omega = 3.1$ eV, respectively [25]. Here, we will only consider WS₂ islands with 0° twist angle. The influence of the twist angle on ultrafast charge separation will be investigated in a separate work.

Figure 1(b) depicts the pump-induced changes of the photocurrent in Fig. 1(a), 240 fs after photoexcitation at $\hbar\omega = 2.0$ eV with a fluence of $F = 1.7$ mJ/cm². Brown and blue

colors indicate a gain and loss of photoelectrons, respectively, with respect to negative pump-probe delay. Figure 1(c) is the same as Fig. 1(b) but for photoexcitation at $\hbar\omega = 3.1$ eV with a fluence of $F = 0.4$ mJ/cm² and 310 fs after photoexcitation. For both excitation energies, we observe gain in the conduction band (CB) of WS₂, gain (loss) above (below) the equilibrium Fermi level in graphene, and a complex gain-loss signal in the WS₂ valence band (VB) with contributions from band shifts and broadening as previously discussed in Refs. [13,18].

To gain access to the transient carrier population of different parts of the band structure, we integrate the photocurrent over the areas marked by the colored boxes in Figs. 1(b) and 1(c). The corresponding pump-probe traces are shown in Fig. 2 together with single-exponential fits (see the Appendix), yielding the decay times τ . Dashed vertical lines in Fig. 2 indicate the pump-probe delay t_{ex} , where the respective pump-probe trace reaches its extremum. The fit results are summarized in Table I. The charge carrier dynamics inside the Dirac cone [Fig. 2(a)] are found to be quite similar for $\hbar\omega = 2.0$ eV and $\hbar\omega = 3.1$ eV, respectively, considering that the pump-pulse cross-correlation (gray-shaded areas in Fig. 2) was longer for $\hbar\omega = 3.1$ eV (90 fs) than for $\hbar\omega = 2.0$ eV (50 fs). The population dynamics of the WS₂ bands, however, show important differences when comparing the two excitation energies. We find that the gain above the equilibrium position of the WS₂ VB [Fig. 2(b)] reaches its maximum ~ 250 fs later for $\hbar\omega = 2.0$ eV than for $\hbar\omega = 3.1$ eV. Further, for $\hbar\omega = 2.0$ eV, the pump-probe signal of the WS₂ CB at K is much bigger than close to Q, indicating that the photoexcited electrons are mainly confined to the K valley [Fig. 2(c1)]. For $\hbar\omega = 3.1$ eV, however, we find that the population of the WS₂ CB at K is smaller than the one close to Q and reaches its maximum ~ 130 fs later [Fig. 2(c2)].

To gain direct access to the timescales for ultrafast charge separation, we extract the related charging-induced band shifts of the WS₂ VB and CB as follows [13,18]. First, we extract energy distribution curves (EDCs) at selected momenta from the trARPES snapshots in Fig. 1, which we fit with an

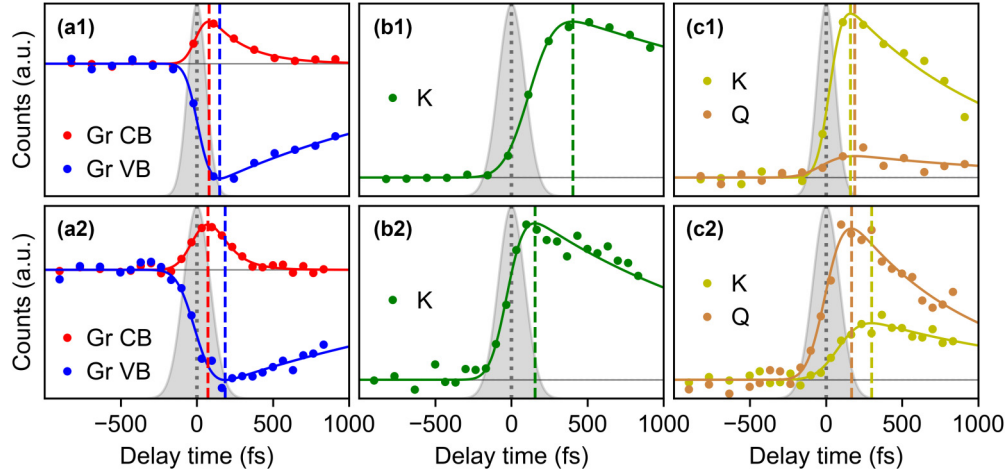


FIG. 2. Population dynamics obtained by integrating the counts over the areas marked by colored boxes in Figs. 1(b) and 1(c). (a) Gain (red) and loss (blue) inside the Dirac cone. (b) Gain above the equilibrium position of the WS₂ VB at K. (c) Population of the WS₂ CB at K (yellow) and close to Q (orange). Rows 1 and 2 present data for excitation at $\hbar\omega = 2.0$ eV and $\hbar\omega = 3.1$ eV, respectively. Continuous lines are single-exponential fits. Dashed colored lines indicate the pump-probe delay where the pump-probe traces reach their respective maximum or minimum. Gray-shaded areas indicate the temporal profile of the pump-probe cross-correlation.

appropriate number of Gaussian peaks (see the Appendix) to obtain the transient binding energies shown in Fig. 3(a). Next, we subtract the transient position of the WS₂ VB from the transient position of the WS₂ CB, yielding the transient band gap E_{gap} shown in Fig. 3(b). Finally, assuming that the band gap changes symmetrically around its center, we add (subtract) half of the transient band gap change $\Delta E_{\text{gap}}/2$ to (from) the transient position of the WS₂ VB (CB) to obtain the shifts $\Delta E_{\text{charge}}^{\text{WS}_2}$ in Fig. 3(c), which we previously attributed to a transient charging of the WS₂ layer with excess electrons [13,18].

The corresponding charging shift of the graphene layer in Fig. 3(d) is obtained by extracting momentum distribution curves (MDCs) that we fit with a Lorentzian (see the Appendix). The resulting peak positions are averaged and multiplied with the slope of the Dirac cone to yield the data points in Fig. 3(d). All orange and blue curves in Fig. 3 are single-exponential fits (see the Appendix), the fit parameters of which are summarized in Table II. Vertical dashed orange and blue lines indicate the positions t_{ex} , where the respective pump-probe signals reach their extrema. Note that the fit for the transient band gap in Fig. 3(b) is sensitive to the value assumed for the equilibrium gap size (we assumed $E_{\text{gap}}^{\text{equ}} = 2.08$ eV), which also affects $\Delta E_{\text{charge}}^{\text{WS}_2}$ in Fig. 3(c). We would like to stress, though, that varying the equilibrium gap size by a reasonable amount has only a minor influence on the data points in Fig. 3(c). Considering this, the behavior of the

transient WS₂ band gap at $k = 1.2 \text{ \AA}^{-1}$ is very similar for $\hbar\omega = 2.0$ eV and $\hbar\omega = 3.1$ eV. In contrast to this, both the WS₂ and the graphene charging shifts are found to depend on the pump photon energy. We find that both charging shifts reach their extrema 160–340 fs later for $\hbar\omega = 2.0$ eV than for $\hbar\omega = 3.1$ eV.

IV. DISCUSSION

The results obtained for $\hbar\omega = 2.0$ eV are in good agreement with previous trARPES results [13,18,26], making their interpretation straightforward. The asymmetric population dynamics of the Dirac cone [Fig. 2(a1)], the gain above the equilibrium position of the WS₂ VB [Fig. 2(b1)], and the charging shifts in Figs. 3(c) and 3(d) provide direct evidence of ultrafast charge separation in the WS₂-graphene heterostructure, where hole transfer from WS₂ to graphene is much faster than electron transfer. The relevant charge transfer states for the WS₂-graphene heterostructure have been previously identified using density functional theory calculations [13]. For convenience, we sketch the relevant part of the band structure in Fig. 4. Charge transfer states, where the WS₂ and graphene bands hybridize, are shown in red. For $\hbar\omega = 2.0$ eV, photoexcitation occurs at the K valley of WS₂. The previously proposed scattering processes resulting in ultrafast charge transfer to the graphene layer are indicated by orange arrows [13,18]. The transient reduction of the band gap in Fig. 3(b)

TABLE I. Fit parameters for single-exponential fits of pump-probe traces shown in Fig. 2.

	Red box Graphene gain	Blue box Graphene loss	Green box Gain above equilibrium position of WS ₂ VB	Yellow box Gain in WS ₂ CB at K	Orange box Gain in WS ₂ CB close to Q
$\tau_{2.0\text{eV}}$	230 ± 40 fs	1.7 ± 0.2 ps	3.2 ± 0.4 ps	1.0 ± 0.1 ps	1.3 ± 0.8 ps
$\tau_{3.1\text{eV}}$	120 ± 30 fs	2.2 ± 0.2 ps	1.5 ± 0.1 ps	0.8 ± 0.1 ps	0.8 ± 0.1 ps
$t_{\text{ex}, 2.0\text{eV}}$	~ 80 fs	~ 150 fs	~ 400 fs	~ 160 fs	~ 190 fs
$t_{\text{ex}, 3.1\text{eV}}$	~ 70 fs	~ 190 fs	~ 160 fs	~ 300 fs	~ 170 fs

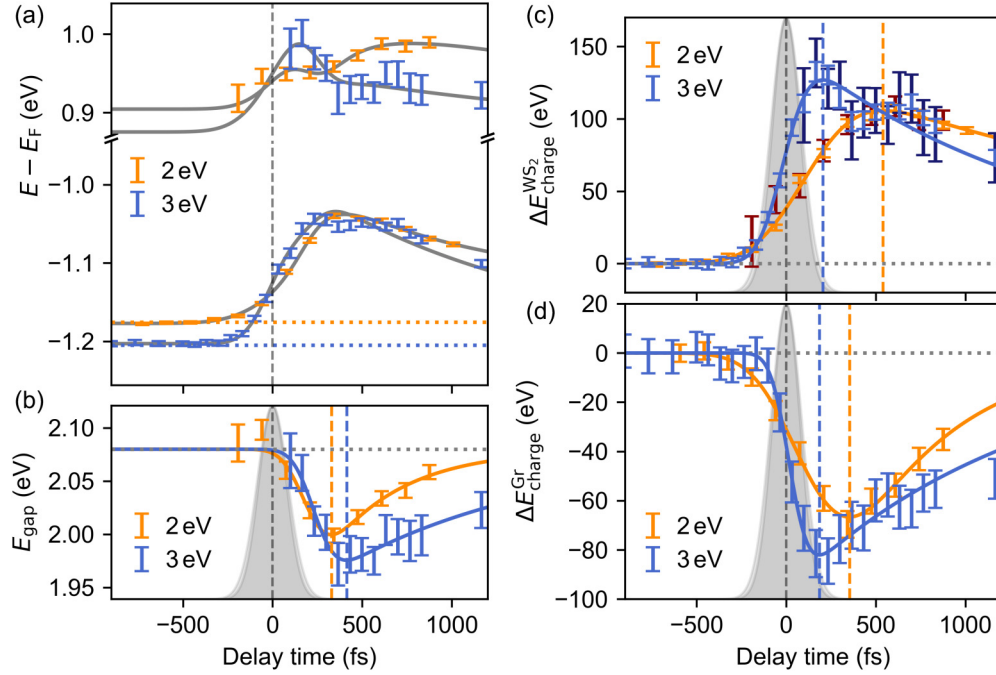


FIG. 3. Transient band structure. (a) Transient band position of WS₂ CB (top) and VB (bottom). (b) Transient band gap. (c) Charging shifts of WS₂ obtained from the VB (blue, orange) and CB (dark blue, red). (d) Charging shift of Dirac cone. Data points for excitation at $\hbar\omega = 2.0$ eV and $\hbar\omega = 3.1$ eV are shown in orange and blue, respectively. Orange and blue curves are single-exponential fits. Gray curves in panel (a) are guides to the eye calculated from the VB fit in panel (a) and the gap fit in panel (b) for the CB, and from the gap fit in panel (b) and the charging shift fit in panel (c) for the VB. Vertical colored dashed lines indicate the pump-probe delay where the pump-probe traces reach their respective maximum or minimum. Gray-shaded areas indicate the temporal profiles of the pump-probe cross-correlations.

has been previously attributed to screening of the Coulomb interaction by photoinduced free carriers [19,27–32].

The observed differences between excitation at $\hbar\omega = 2.0$ eV and $\hbar\omega = 3.1$ eV, however, deserve further discussion. We start with the observation that, for $\hbar\omega = 3.1$ eV, the population dynamics in the WS₂ CB in Fig. 2(c2) are different at K and close to Q. The 3.1 eV pump pulse directly populates states close to the Q valley [see Fig. 1(a)] [25]. These carriers are then observed to scatter to the K valley within ~ 130 fs ([Fig. 2(c2)] in good agreement with previously reported intervalley scattering times for WS₂ and similar transition metal dichalcogenides [33–37].

Next, we focus on the observation that the gain above the equilibrium position of the WS₂ VB [Fig. 2(b)] and the charging shifts [Figs. 3(c) and 3(d)] are found to reach their extrema at earlier time delays for $\hbar\omega = 3.1$ eV than for $\hbar\omega = 2.0$ eV. This indicates that hole transfer is faster for $\hbar\omega = 3.1$ eV than for $\hbar\omega = 2.0$ eV. From Ref. [18], it is known that the

rates for charge transfer from WS₂ to graphene increase with increasing electronic temperature as it becomes easier for the photoexcited carriers to overcome the energy barriers to the closest charge transfer states.

The transient electronic temperature for the WS₂ layer is difficult to determine due to the limited signal-to-noise ratio. Therefore, we estimate the peak electronic temperatures for electrons and holes in WS₂ as described in detail in the Appendix. We obtain $T_{\max}^{3.1\text{ eV}} \sim 3700$ K $>$ $T_{\max}^{2.0\text{ eV}} \sim 1000$ K as the excess energy $\frac{1}{2}(\hbar\omega - E_{\text{gap}})$ of the carriers is considerably larger at $\hbar\omega = 3.1$ eV. This, indeed, makes it easier for the holes to overcome the energy barrier $\Delta E_K \sim 170$ meV (see Fig. 4). In addition, $T_{\max}^{3.1\text{ eV}}$ is high enough for the holes to reach the second charge transfer state at $Q < k < K$ in the VB with an energy barrier of $\Delta E_{QK} \sim 410$ meV. Hole transfer at $Q < k < K$ is expected to be faster than at $k > K$ because the size of the avoided crossing between WS₂ VB and graphene Dirac cone is bigger (and therefore hybridization is stronger)

TABLE II. Fit parameters for single-exponential fits of pump-probe traces shown in Fig. 3.

	WS ₂ VB position	E_{gap}	$\Delta E_{\text{charge}}^{\text{WS}_2}$	$\Delta E_{\text{charge}}^{\text{Gr}}$
$\tau_{2.0\text{ eV}}$	1.5 ± 0.2 ps	0.4 ± 0.2 ps	2.7 ± 0.9 ps	0.6 ± 0.1 ps
Amplitude _{2.0 eV}	137 ± 6 meV	80 ± 30 meV	110 ± 10 meV	70 ± 10 meV
$\tau_{3.1\text{ eV}}$	1.3 ± 0.1 ps	1.2 ± 0.2 ps	1.5 ± 0.2 ps	1.3 ± 0.1 ps
Amplitude _{3.1 eV}	169 ± 8 meV	104 ± 8 meV	127 ± 6 meV	82 ± 3 meV
$t_{\text{ex}, 2.0\text{ eV}}$	~ 350 fs	~ 330 fs	~ 540 fs	~ 350 fs
$t_{\text{ex}, 3.1\text{ eV}}$	~ 400 fs	~ 410 fs	~ 200 fs	~ 190 fs

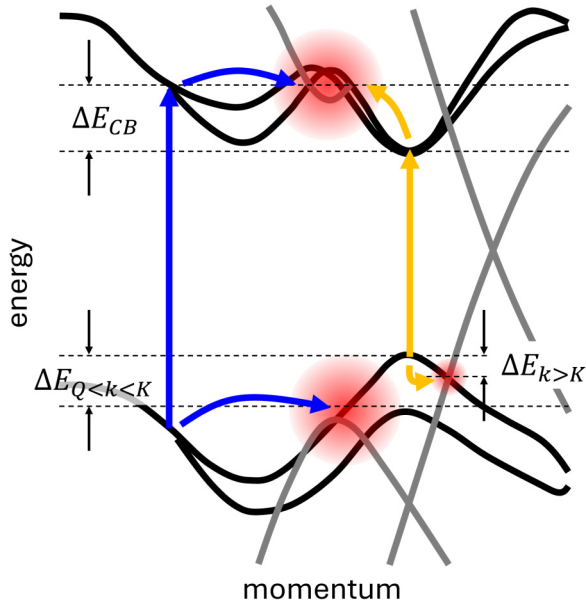


FIG. 4. Schematic of quantum pathways for ultrafast charge transfer. The band structure sketch is based on density functional theory calculations from Ref. [13]. The color code indicates whether the wave function is localized on the graphene layer (gray curves), the WS₂ layer (black curves), or delocalized over both layers (red dots). Blue (orange) arrows indicate direct optical transitions excited at $\hbar\omega = 3.1$ eV ($\hbar\omega = 2.0$ eV) and subsequent carrier relaxation via different charge transfer states.

[13]. The excitation and charge transfer channels for $\hbar\omega = 3.1$ eV are indicated by blue arrows in Fig. 4.

Note that the photoexcited carrier densities (an estimate is provided in the Appendix) exceed the Mott threshold [28,38,39], where photoexcited excitons decay into free electron-hole pairs within ~ 100 fs [40]. The decay of excitons into free electrons and holes results in a delayed onset of the band gap renormalization in Fig. 3(b) with respect to the conduction band population in Fig. 2(c) (see the Appendix). However, our data analysis allows us to distinguish between effects caused by screening [transient reduction of the band gap in Fig. 3(b)] and charge separation [relative shift between the center of the WS₂ band gap and the Dirac point in graphene in Figs. 3(c) and 3(d)]. Therefore, we believe excitonic effects to be of minor importance for discussing ultrafast charge transfer phenomena in the present work.

Finally, we would like to briefly comment on the possible influence of ultrafast energy transfer between WS₂ and graphene. Following photoexcitation of vdW heterostructures, both charge and energy transfer are possible relaxation channels. While the charging shifts in our data provide direct evidence of ultrafast charge separation and thus ultrafast charge transfer, indications for ultrafast energy transfer are less obvious. Note that our data show none of the indications of Meitner-Auger energy transfer discussed in Ref. [41]. A possible contribution of Förster energy transfer [42] is difficult to evaluate from our data. However, we would like to point out that the presence or absence of additional energy transfer does not affect our conclusions regarding ultrafast charge transfer.

V. SUMMARY AND OUTLOOK

In summary, we used trARPES of a WS₂-graphene heterostructure to show that the elevated carrier temperature following C-exciton excitation activates a second, highly efficient charge transfer channel for holes. These results show that charge separation across vdW interfaces can be controlled via the incident pump photon energy, opening up strategies to optimize the performance of vdW heterostructures for future applications in light harvesting and detection.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX

This Appendix contains information about the data analysis including fitting functions, an estimate of the transient carrier temperature in WS₂ and a comment on the decay of excitons into free electrons and holes.

1. Exponential decay fits

To extract rise and decay times of a given pump-probe signal, we use the following analytic fitting function that stems from convolving a step function with exponential decay for the underlying dynamics with a Gaussian accounting for the finite temporal resolution:

$$f(t) = \frac{a}{2} \left(1 + \operatorname{erf} \left(\frac{(t - t_0)\tau - \frac{\text{FWHM}^2}{8 \ln 2}}{\sqrt{2}\tau \frac{\text{FWHM}}{2\sqrt{2 \ln 2}}} \right) \right) \times \exp \left(\frac{\frac{\text{FWHM}^2}{8 \ln 2} - 2(t - t_0)\tau}{2\tau^2} \right). \quad (\text{A1})$$

Here, a is the amplitude, erf is the error function, FWHM is the full width at half maximum of the Gaussian, t_0 is the time delay where pump and probe overlap, and τ is the decay time. This function was used to fit the time traces in Figs. 2 and 3.

2. Extracting transient peak positions

For extracting the transient position of the WS₂ valence band, the data in Fig. 5(a) were integrated over the momentum range $\Delta k = \pm 0.04 \text{ \AA}^{-1}$ for 2.0 eV and $\Delta k = \pm 0.06 \text{ \AA}^{-1}$ for

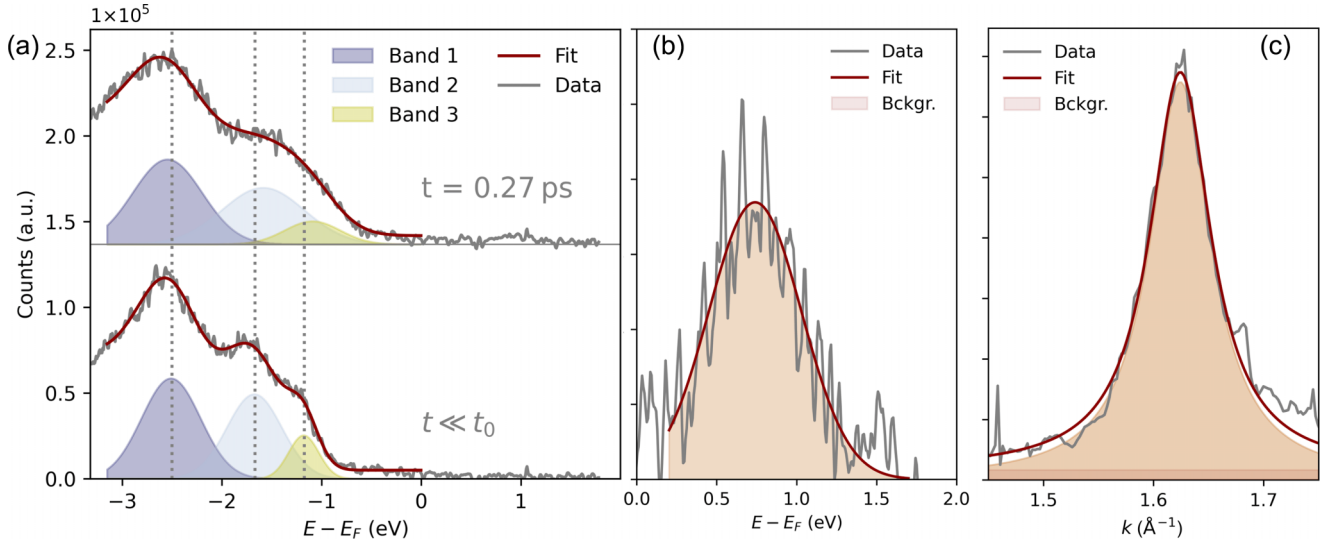


FIG. 5. Extracting transient peak positions. (a) WS₂ EDCs for negative pump-probe delay and at $t = 0.27$ ps fitted with a constant offset and three Gaussian peaks. The dotted vertical lines mark the peak positions for negative pump-probe delay. (b) Pump-induced changes of the EDC through the WS₂ conduction band together with a Gaussian fit. (c) MDC through the graphene Dirac cone at negative pump-probe delay fitted with the sum of a constant offset and a Lorentzian peak.

3.1 eV around $k = 1.2 \text{ \AA}^{-1}$. The latter was chosen to ensure that the graphene valence band does not influence the data. The resulting energy distribution curves were then fitted with a constant background and three Gaussian peaks for the three expected bands. Exemplary fits are presented in Fig. 5(a). The following constraints were applied:

- (1) The constant background was fixed to the value found for negative pump-probe delay.
- (2) The energy difference between the two spin-split WS₂ valence bands was fixed to the value found for negative pump-probe delay.
- (3) The spectral weight of bands 1 and 2 was fixed to the value found for negative pump-probe delay.

To obtain the transient position of the WS₂ conduction band, the data in Figs. 1(b) and 1(c) were integrated over the momentum range $\Delta k = \pm 0.1 \text{ \AA}^{-1}$ around $k = 1.3 \text{ \AA}^{-1}$. The resulting EDCs were then fitted with a background-free Gaussian [see Fig. 5(b)].

The shift of the graphene Dirac cone was determined by integrating the data in Fig. 1(a) over the energy range $\Delta E = \pm 25$ meV around the five energy positions ($E - E_F$) = -1.0, -0.8, -0.6, -0.4, -0.2 eV. To improve the signal-to-noise ratio, we grouped the resulting MDC data into bins of three consecutive time delays. The final MDCs were fitted by the sum of a constant background and a Lorentzian peak [see Fig. 5(c)] for every energy position. The five momentum shifts obtained in this way were averaged and then converted into an energy shift by multiplying with the slope of the π band of $7 \text{ eV \AA}$.

3. Estimating transient carrier temperatures in WS₂

According to Ref. [43], the absorption in the relevant fluence regime is highly nonlinear. The excited carrier density for resonant excitation of the C exciton with a fluence of 0.4 mJ/cm^2 can be directly obtained from Ref. [43] as $n_{\text{ex}} \sim 1 \times 10^{14} \text{ cm}^{-2}$. Reference [43] also showed that absorption at

the A-exciton resonance drops to zero when similar carrier densities are reached. Therefore, we assume that both 2.0 and 3.1 eV excitation generate carrier densities on the order of $n_{\text{ex}} \sim 1 \times 10^{14} \text{ cm}^{-2}$ even though the incident fluences differ considerably.

To estimate the peak carrier temperature, we first assume that the excess energy for electrons and holes $E_{\text{excess}} \sim \frac{1}{2}(\hbar\omega_{\text{pump}} - E_{\text{gap}})$ can be directly converted into a carrier temperature $k_B T$. The excess energy for 3.1 eV excitation is 500 meV, yielding $T_{3.1 \text{ eV}} \sim 5800 \text{ K}$. The A-exciton resonance, however, lies below the single-particle gap. In our case, the photoexcited carrier densities exceed the Mott threshold, such that the excitons rapidly decay into free electron-hole pairs. These free electron-hole pairs screen the Coulomb interaction which results in a transient reduction of the single particle band gap by ~ 80 meV [see Fig. 3(b)]. Therefore, it seems justified to assume that, for 2.0 eV excitation, electrons and holes gain an excess energy of ~ 40 meV, yielding a transient carrier temperature of $T_{2.0 \text{ eV}} \sim 500 \text{ K}$.

An improved estimate can be obtained by calculating the carrier temperature in the framework of the quasifree electron model. Here, the change of the internal energy due to heating of a given carrier density n_{ex} from room temperature to an arbitrary temperature T is given by

$$\Delta U = \int_{E_{\text{CB}=0}}^{\infty} E \times \text{DOS}(E) \times f_{\text{FD}}(E, \mu, T) dE - \int_{E_{\text{CB}=0}}^{\infty} E \times \text{DOS}(E) \times f_{\text{FD}}(E, \mu, T = 300 \text{ K}) dE,$$

where the 2D $\text{DOS}(E) = \frac{m^* g_s g_v}{2\pi \hbar^2}$. $g_s = 2$ and $g_v = 2$ are the spin and valley degeneracies, respectively. From the carrier concentration n_{ex} , we obtain the chemical potential $\mu = \frac{2\pi \hbar^2}{m^* g_s g_v} n_{\text{ex}}$ that, in Sommerfeld approximation, is independent of temperature. The part of the absorbed fluence that is available for heating the carriers is given by the product of

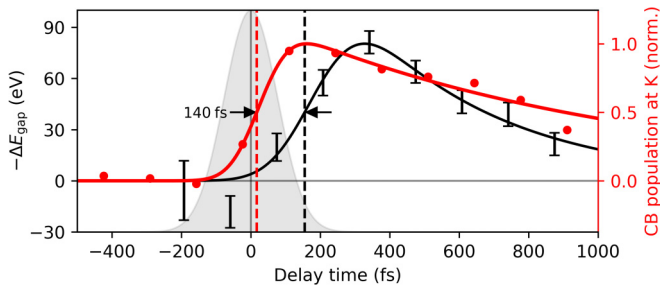


FIG. 6. Excitonic effects. Direct comparison between transient band gap reduction $-\Delta E_{\text{gap}}$ (black) and conduction band population (red) for resonant excitation of the A exciton. The offset between the two rising edges of ~ 140 fs is caused by the decay of excitons into free electrons and holes.

the photoexcited carrier density n_{ex} and the excess energy E_{excess} . From $n_{\text{ex}} E_{\text{excess}} = \Delta U$, we obtain $T_{2.0\text{ eV}} \sim 1000$ K and $T_{3.1\text{ eV}} \sim 3700$ K for an effective mass of $m^* = 0.5m_e$.

4. Decay of excitons into free electrons and holes

The estimated carrier densities on the order of $n_{\text{ex}} \sim 1 \times 10^{14} \text{ cm}^{-2}$ exceed the Mott threshold and are expected to decay into free electrons and holes within ~ 100 fs [40]. Free charge carriers efficiently screen the Coulomb interaction and are responsible for the transient reduction of the band gap reported in Fig. 3(b). The decay of excitons into free electrons and holes shows up as a delayed onset of the band gap renormalization with respect to the transient population of the conduction band in Fig. 6.

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