Laser-Controlled Charge Transfer in a Two-Dimensional Organic/Inorganic Heterostructure

Matheus Jacobs,* † Jannis Krumland, † and Caterina Cocchi,* † ‡

†Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany
‡Institute of Physics, Carl von Ossietzky Universität Oldenburg, 26129 Oldenburg, Germany

E-mail: jacobs@physik.hu-berlin.de; caterina.cocchi@uni-oldenburg.de
Abstract

Understanding the fundamental mechanisms ruling laser-induced charge transfer in hybrid organic/inorganic materials is of paramount importance to exploit these systems in next-generation opto-electronic applications. In a first-principles work based on real-time time-dependent density-functional theory, we investigate the ultrafast charge-carrier dynamics of a prototypical two-dimensional heterostructure formed by a MoSe$_2$ monolayer doped by adsorbed pyrene molecules. By varying the intensity of the incident pulse, set in resonance with the frequency of the lowest-energy transition in the physisorbed moieties, we monitor charge- and energy-transfer during and immediately after femtosecond irradiation. In the linear regime triggered by weak laser intensities, charge transfer occurs from the molecules to the inorganic monolayer. Conversely, under strong pulses, when the response of the hybrid material becomes markedly non-linear, the direction of charge transfer is reverted, with electrons being transferred from MoSe$_2$ to pyrene. This finding is explained in terms of Pauli blocking: laser-induced (de)population of (valence) conduction states saturates for intensities beyond 200 GW/cm$^2$. A thorough analysis of electronic current density, excitation energy, and number of excited electrons supports this interpretation.

Keywords

Ultrafast dynamics; time-dependent density-functional theory; transition metal dichalcogenides; hybrid interfaces; charge transfer; electronic coherence.
1 Introduction

The possibility to control the electronic structure of materials via ultrashort laser pulses has attracted considerable interest in the last couple of decades. This perspective has become particularly appealing for hybrid inorganic/organic interfaces, where the enhanced light-harvesting abilities of carbon-conjugated molecules are combined with the efficient charge-carrier mobility of inorganic semiconductors. Depending on the physico-chemical properties of the constituents and on the nature of their mutual interactions, in these systems, charge transfer can be achieved already in the ground state or it can be triggered in the excited state by the action of a laser.

The choice of transition-metal dichalcogenide (TMDC) monolayers as inorganic substrates for hybrid interfaces is particularly advantageous, due to the band-gap size of these materials, their large carrier mobility, as well as their extraordinary light-matter couplings even in the ultrafast regime. Decorating these systems with organic molecules has opened additional pathways to tune their properties. Recent experiments have demonstrated that, by exciting TMDC-based hybrid interfaces with a laser pulse, it is possible to induce electron or hole transfer depending on the level alignment between the components. In materials with such complex electronic structures, this finding unveils intriguing opportunities to generate laser-induced photocurrents by modulating the characteristics of the pulse. By tuning the laser frequency, one could selectively excite a specific electronic transition and resonantly inject charge carriers to the conduction band. Furthermore, control over the field intensity enables adjusting the amount of energy transferred to the system as well as the number of photoexcited electrons and holes.

While the manipulation of material properties via laser irradiation is potentially accessible with the state-of-the-art experimental setups, its successful realization requires in-depth knowledge of the electronic structure of the interface as well as thorough understanding of the microscopic mechanisms governing the response of the system to the external perturbation. \textit{Ab initio} methods based on real-time time-dependent density-functional theory
(RT-TDDFT) are ideally suited for this task, as they enable monitoring sub-picosecond electron dynamics with full control over the characteristics of the incident electric pulse (shape, duration, intensity, etc.) and its temporal evolution.\textsuperscript{10,28–30}

In this work, we investigate the laser-induced charge-carrier dynamics of a prototypical inorganic/organic heterostructure formed by a MoSe\textsubscript{2} monolayer decorated with physisorbed pyrene molecules. In the framework of RT-TDDFT, we excite the hybrid interface with a femtosecond Gaussian-enveloped pulse of varying intensity and with frequency in resonance with the lowest-energy electronic transition in the molecule. Under weak laser irradiation, when the response of the system is linear, electronic charge is transferred from pyrene to MoSe\textsubscript{2}. Increasing the field intensity drives the system into the nonlinear regime, where characteristic effects such as high-harmonic generation as well as sublinear increase of excitation energy and number of excited electrons manifest themselves. Furthermore, excited by laser intensities higher than 100 GW/cm\textsuperscript{2}, electrons flow from the TMDC to the molecules, opposite to the scenario realized in the linear regime. We rationalize these findings in terms of intensity-dependent, laser-induced saturation of valence and conduction band populations, whereby the reverted direction of charge transfer from the linear to the nonlinear regime is regimented by Pauli blocking.

2 Results

The starting point of our study is the ground-state electronic structure of the two-dimensional pyrene/MoSe\textsubscript{2} heterostructure. We model this system by considering a pyrene molecule physisorbed on a 4×4 supercell of the MoSe\textsubscript{2} monolayer (see Figure 1a). In this setup, each molecule is separated by at least 5 Å from its closest replica in the (x, y) plane, thereby minimizing intermolecular interactions. The band structure computed for the hybrid system is unfolded in the Brillouin zone of MoSe\textsubscript{2} and represented with the aid of a spectral function;\textsuperscript{31} in the corresponding density of states (DOS), the contributions of pyrene are
projected out to better identify the energy level associated to this subsystem (Figure 1b).

The level alignment at the interface is of type I: the highest occupied molecular orbital (HOMO) of the molecule gives rise to a dispersionless level a few tens of meV below the valence band maximum (VBM) of MoSe$_2$ at K. The conduction band minimum pertains to the inorganic component as well, giving rise to a direct band gap at K for the hybrid system. No signs of hybridization appear between the HOMO and the highest valence band of the TMDC. On the other hand, both the HOMO-1 as well as the lowest unoccupied molecular orbital (LUMO) of pyrene are clearly hybridized with the valence and conduction bands of the TMDC around ±1.5 eV, respectively. Signatures of other occupied and virtual molecular orbitals coupling with MoSe$_2$ bands are visible in Figure 1b; the conditions under which these interactions occur are systematically discussed in Ref. 31.

The type-I level alignment of the pyrene/MoSe$_2$ heterostructure, with the larger gap pertaining to the molecule (Figure 1b), suggest favorable conditions for laser-induced charge transfer across the interface. Due to the strong excitonic effects dominating the absorption onset of TMDC monolayers, one may anticipate photo-induced charge separation to be more efficient above the optical gap, in the region where free-carrier excitations take place. For this reason, we impinge the hybrid system with a laser pulse of Gaussian shape, approximately 10 fs duration, and carrier frequency $\hbar \omega_0 = 3.1$ eV in resonance with the electronic transition between the HOMO and the LUMO of pyrene (see Supporting Information, SI, Figures S1 and S2; Table S1). It should be noted, however, that both molecular orbitals are in close proximity with MoSe$_2$ bands and especially the LUMO is clearly hybridized with them.

We investigate the electronic dynamics of the hybrid system in an ultrashort time window of 30 fs in total, i.e., up to 20 fs after the pulse is switched off. First, we inspect the electric current density, $J(t)$ (Eq. 5), induced by the external field to the pyrene/MoSe$_2$ heterostructure. With this quantity, we can monitor the response of the system to the time-dependent perturbation of varying peak intensities, ranging from $I = 2 \times 10^{11}$ W/cm$^2$
Figure 1: a) Ball-and-stick representation of the pyrene/MoSe$_2$ interface considered in this work, where Mo atoms are depicted in turquoise, Se atoms in yellow, C atoms in grey, and H atoms in white: side view (upper panel) and top view (lower panel). b) Unfolded band structure of the system plotted in the unit cell of MoSe$_2$ with the aid of the spectral function (left, color bar on top) and corresponding density of states (right) with the projected out contributions of pyrene in purple.

To $I = 5 \times 10^{12} \text{ W/cm}^2$ (see Figure 2). During the first $\sim 10 \text{ fs}$, when the laser is on, the induced current builds up, exhibiting an oscillatory behavior resembling the one of the applied field, with amplitude varying according to the intensity of the latter. At later times, when the external perturbation is turned off, the induced current density exhibits weaker, residual oscillations, which are a signature of the remaining coherence between ground- and excited-states. For the weakest considered intensities, the envelope of such oscillations and its periodicity of approximately 15 fs is visible in Figure 2a,b. Under the action of stronger
pulses, the amplitude of these residual oscillation is considerably reduced and a periodic pattern of their envelope is hardly recognizable (Figure 2c,d). This behavior is associated with the non-linear response of the system.\textsuperscript{34}

To better clarify the nature of nonlinear processes that are in play in the considered system, we compute the harmonic spectrum, $J(\omega)$, which corresponds to Fourier transform of the time derivative of the electric current density (see Eq. 6). Inspection of Figure 3 reveals that the weakest pulse excites only the fundamental harmonic corresponding to the natural carrier frequency, $\omega_0 = 3.1$ eV. In the spectrum obtained for $I = 1 \times 10^{12}$ W/cm$^2$, maxima are present up to $\omega_2 = 9.3$ eV. As the intensity increases further, higher harmonics are generated up to $\omega_4 = 15.5$ eV under irradiation with $I = 2 \times 10^{12}$ W/cm$^2$, and up to $\omega_6 = 21.7$ eV for $I = 5 \times 10^{12}$ W/cm$^2$, which falls beyond the range displayed in Figure 3. The appearance of higher harmonics confirms the nonlinear regime of interaction between the system and the laser pulses with intensities above $10^{12}$ W/cm$^2$. Analogous behavior was identified in bulk materials investigated with the same theoretical formalism.\textsuperscript{28,30,37}

In the next step of our analysis, we monitor the excitation energy, $\Delta E_{ex}(t) = E(t) -$
Figure 3: High-harmonic generation spectrum, $J(\omega)$, for the pyrene/MoSe$_2$ heterostructure impinged by pulses of increasing intensities. Vertical lines represent the fundamental carrier frequency ($\omega_0$) and its overtones ($\omega_n$ with $n = 1, \ldots, 5$).

$E(t = 0)$, calculated as the difference between the electronic energy at a certain time $t > 0$ and in the ground state.$^{38,39}$ In Figure 4a, we display this quantity calculated at $t = 30$ fs for increasing pulse strengths. The time evolution for selected intensities is shown in Figure 4b following the respective color code. Corresponding graphs referred to the gray dots in Figure 4a are reported in the SI, Figure S3. The relation between the excitation energy and the laser intensity suggests linear response for $I = 2 \times 10^{11}$ W/cm$^2$, where $\Delta E_{ex}(t = 30) = 0.18$ eV/atom, and for $I = 10^{12}$ W/cm$^2$, where this value increases up to 0.77 eV/atom (see Figure 4a). A deviation from linearity is seen starting from $I = 2 \times 10^{12}$ W/cm$^2$: in this case, the transferred energy in 30 fs increases only to 1.15 eV/atom. By further enhancing the laser intensity, the excitation energy keeps growing almost linearly but with a reduced slope compared to the one corresponding to the weaker pulses, reaching the value of 2.18 eV/atom at the end of the simulation window when $I = 5 \times 10^{12}$ W/cm$^2$. The time evolution of $\Delta E_{ex}(t)$ (Figure 4b) shows that after a short transient window of approximately 10 fs, coinciding
Figure 4: Excitation energy $\Delta E_{ex}(t) = E(t) - E(t = 0)$ as a function of the laser intensity a) with $t = 30$ fs and b) within the entire temporal range considered in these simulations. Number of excited electrons, $N_{ex}(t)$ c) with $t = 30$ fs and d) within the entire temporal range considered in these simulations. In panels b) and d), the energy of the incident field is displayed in the background by a solid black line. In panel c), the dotted line indicates the hypothetical behavior of the system if the linear regime were maintained at increasing laser intensities.

with the building-up of the pulse (black line in the background) in which this quantity grows rapidly, it forms a plateau, where it remains indefinitely in the absence of dissipation effects. The maximum value reached by $\Delta E_{ex}(t)$ during its evolution shows an intensity-dependent profile, consistent with the trends shown in Figure 4a. A similar behavior for $\Delta E_{ex}(t)$ was seen also in conventional bulk semiconductors and insulators, investigated at the same level of theory.\[36\]

Additional information about the response of the hybrid system to the applied laser perturbation can be collected from the number of excited electrons $[N_{ex}(t)$, see Eq. (7)] within the considered 30 fs temporal range. $N_{ex}(t = 30$ fs) exhibits a more pronounced nonlinear dependence with respect to the laser intensity compared to the excitation energy computed at the end of the simulation window. To guide the readers, in Figure 4c, a dotted line marks the expected number of excited electrons in the hypothetical scenario in which the entire process occurred in the linear regime. In such a case, $N_{ex} = \Delta E_{ex}/\hbar \omega_0$, where the
carrier frequency $\omega_0$ equals the average photon frequency. In the considered pyrene/MoSe$_2$ interface, $N_{ex}$ follows this linear behavior up to $I = 1 \times 10^{12}$ W/cm$^2$, in agreement with the trend exhibited by $\Delta E_{ex}$ (Figure 4a). For intensities equal or higher than $I = 2 \times 10^{12}$ W/cm$^2$, the system is driven out of the linear regime: for $I = 5 \times 10^{12}$ W/cm$^2$, the number of excited electrons per atom is almost halved with respect to the hypothetical linear-response scenario (Figure 4c). The behavior of $N_{ex}(t)$ plotted in Figure 4d is similar the one of $\Delta E_{ex}(t)$ in Figure 4b: the value of the observable increases steeply with the ramping up of the pulse and reaches its maximum around 8 fs, after which the plateau is formed.

With the knowledge gained so far from the analysis of the electric current density, of the excitation energy, and of the number of excited electrons, we are equipped to inspect the charge-transfer dynamics at the hybrid pyrene/MoSe$_2$ interface. These results are obtained from a time-dependent Bader charge analysis performed throughout the considered 30 fs time window of laser-induced dynamics. The hybrid system is partitioned into its inorganic (MoSe$_2$) and organic (pyrene) components, and the partial charges are offset with respect to their ground-state value: as a result of the electronic interactions between the molecule and the monolayer, we find a slight electron excess of 0.01 e on MoSe$_2$. This value is of the same order of magnitude as the ground-state charge-transfer computed for molecules with recognized abilities as donors or acceptors adsorbed on a TMDC monolayer. However, it is 10 times smaller than the amount of charge withdrawn by a strong organic acceptor from a silicon surface.

When the system is excited by the weakest considered pulse with $I = 2 \times 10^{11}$ W/cm$^2$, a charge transfer of 0.06 e occurs from the molecule to the TMDC (see Figure 5a). While this finding appears to be consistent with the type-I level alignment exhibited by the interface (Figure 1b), we emphasize that in our simulations charge transfer takes place uniquely as an effect of laser irradiation and is not mediated by subsequent scattering events (e.g., due to electron-phonon coupling) redistributing electrons and holes within the bands. With a pulse intensity of $I = 1 \times 10^{12}$ W/cm$^2$, the charge transfer towards MoSe$_2$ is enhanced up to
Figure 5: Time-dependent variation of the Bader partial charges with respect to the ground-state value (Δq) at increasing laser intensities. In the analysis, the hybrid interface is partitioned into its inorganic (MoSe$_2$) and organic component (pyrene). Positive (negative) values indicate electron accumulation (depletion). Gray areas represent the time-window in which the laser is active. The fainted lines fit of the raw data (colored dots) as a guide for the eyes.
a maximum of 0.10 e, which is reached right after the laser is switched off (see Figure 5b). Overall, the time-dependent Bader charges exhibit a beating pattern resulting from the system being in a coherent superposition of multiple excited states. This finding is consistent with the behavior of the electric current density seen in Figure 2. On the other hand, the fast oscillations that are visible in the raw data (blue and red dots) in Figure 5a,b have the frequency of the laser and are thus related to the ground-state/excited-state coherence.

When the laser intensity is doubled, reaching the value of $2 \times 10^{12}$ W/cm², the aforementioned scenario starts to change (Figure 5c). The application of the pulse initially promotes electron transfer from the molecule to the TMDC. However, as soon as the perturbation is turned off, the partial charges on pyrene (MoSe₂) start to change from negative to positive (positive to negative) exhibiting baseline oscillations, as a fingerprint of excited-state/excited-state coherence. At the end of the considered 30 fs time-window, no effective charge transfer has occurred and each subsystem is left in an essentially charge-neutral state. The most intense of the considered lasers ($I = 5 \times 10^{12}$ W/cm²) gives rise to a completely different response of the system with respect to the previously analyzed cases (Figure 5d): 0.1 electrons are transferred from the molecule to the TMDC within approximately 17 fs; subsequent oscillations appear but the excess of electrons (holes) on pyrene (MoSe₂) remains in the considered time window of 30 fs. This behavior can be additionally visualized through the charge density difference computed at the end of the simulations with respect to the ground-state value (see Figure S4 in the SI).

To clarify which mechanisms drive the intensity-dependent charge transfer across the pyrene/MoSe₂ heterostructure, we analyze the time-dependent occupation density (Eq. 8) at the end of the 30 fs time window considered in our simulations (see Figure 6). This quantity can be qualitatively contrasted against the total DOS of the hybrid interface and the projected contributions of pyrene (see also Figure 1b), in order to identify those states that are mainly involved in the excitation process. For visualization purposes, in Figure 6 both depopulation and occupation are indicated by positive peaks below and above the Fermi
Figure 6: Occupation density (colored lines) computed at the end of the time-dependent simulations (30 fs) at increasing laser intensities. Maxima below (above) zero, where the Fermi energy is set, indicate laser-driven depopulation (population) of the electronic states. The gray area and the dotted line show the total density of states (TDOS) of the hybrid interface and the projection of the states with pyrene character (PDOS), respectively. Inset: zoom-in of the valence region. A broadening of 35 meV is applied to all displayed quantities.

When the laser-excited system is in the linear regime \((I = 2 \times 10^{11} \text{ W/cm}^2\), red curve in Figure 6\), a number of valence states, including the HOMO and, in particular, the HOMO-1 of the molecule, which is clearly hybridized with valence bands of MoSe\(_2\) (see Figure 1b), are partly depopulated. Corresponding occupation of conduction states is seen above the absolute minimum, involving bands either with exclusive MoSe\(_2\) character (e.g., around 1.1 eV in Figure 6), as well as hybridized with pyrene orbitals, e.g., with the LUMO, slightly above 1.5 eV. These trends are enhanced under increasing pulse intensity. When the system is hit by lasers with \(I = 1 \times 10^{12} \text{ W/cm}^2\) and \(I = 2 \times 10^{12} \text{ W/cm}^2\) (blue and green curves in Figure 6, respectively), the valence region is remarkably depopulated. In the energy region between -1 eV and -2 eV, the depopulation of both the HOMO and the HOMO-1 of pyrene together with the neighboring states with MoSe\(_2\) character is evident. Moreover, incipient depopulation of the HOMO-2 of the molecule around -2.2 eV can be seen as well. In the conduction region, a sharp increase in the occupation density up to 2 eV is visible.
The sharp maximum at \( \sim 1.2 \) eV, corresponding to pure MoSe\(_2\) states, keep increasing from \( I = 1 \times 10^{12} \) W/cm\(^2\) to \( I = 2 \times 10^{12} \) W/cm\(^2\). Conversely, higher-energy peaks centered at 1.6 eV, where the LUMO of pyrene is located, and at 2 eV, where another state of exclusive MoSe\(_2\) nature is found, appear to be saturated for \( I = 2 \times 10^{12} \) W/cm\(^2\). Finally, under the action of the most intense pulse \( I = 5 \times 10^{12} \) W/cm\(^2\), magenta curves in Figure 6, a broader energy-window of valence and conduction states participate in the excitation. While the maxima between -1.8 eV and -1.0 eV in the occupation density slightly decrease in magnitude compared to their counterparts seen with weaker pulses, as a sign of achieved saturation, valence states between -2 eV and -3.5 eV start being depopulated. Notably, in this region, a number of pyrene orbitals appear. In the conduction band, the occupation of the MoSe\(_2\) band around 1.1 eV further increases as a function of the pulse intensity, although the small variation with respect to the result obtained for \( I = 2 \times 10^{12} \) W/cm\(^2\) hints toward saturation. On the other hand, higher-energy states including the LUMO of pyrene and the TMDC band close to 2 eV do not gain further population. Additional unoccupied pyrene orbitals above 2.5 eV are instead involved in the excitation under the effect of this intense irradiation.

3 Discussion

The analysis presented so far enables us to disclose the intensity-dependent response of the pyrene/MoSe\(_2\) heterostructure excited by a femtosecond laser pulse. For impinging fields up to \( I = 1 \times 10^{12} \) W/cm\(^2\), the response of the system is linear, as testified by the relation between excitation energy and laser intensity (see Figure 4); the same holds true also for the number of excited electrons per atom. For intensities equal or larger than \( I = 2 \times 10^{12} \) W/cm\(^2\), the hybrid system is driven to the nonlinear regime, as shown by the higher order harmonics in the corresponding spectrum (Figure 3). However, the most striking intensity-dependent behavior is exhibited by the charge-transfer dynamics across the interface (Figure 5). Under
weak irradiation, pyrene behaves as a donor and MoSe$_2$ as an acceptor, compatible with the type-I level alignment exhibited by this heterostructure in the ground state (see Figure 1b). Stronger perturbations alter this behavior, either effectively inhibiting interfacial charge transfer via charge-density oscillations, or by reverting the direction of charge transfer, as seen for the most intense lasers considered in our simulations.

Figure 7: Pictorial sketch of the charge-transfer mechanisms occurring in the pyrene/MoSe$_2$ heterostructure. (Left) When the system is excited by a weak pulse, the response of the system is linear with respect to the external field and the dominant mechanism is the electron transfer from the molecule to the TMDC. (Right) Upon stronger intensity driving the system in the nonlinear regime, the lowest unoccupied states of the system are saturated and the resulting direction of the charge transfer is reversed.

This behavior can be understood from the occupation density of the electronic states during the laser-induced time evolution (Figure 6). When weak pulses impinge the hybrid system, electrons are transferred from the organic to the inorganic side of the interface on account of the pulse-driven depopulation of HOMO and of the HOMO-1 of pyrene (see Figure 7, left panel). This process, however, approaches saturation already with the medium laser intensities employed in these simulations. Under strong laser irradiation, pyrene→MoSe$_2$ transitions are bleached and Pauli blocking inhibits charge transfer from the molecule to the monolayer. In contrast, MoSe$_2$→MoSe$_2$ and especially MoSe$_2$→pyrene excitations take place in this scenario, leading to a depletion (accumulation) of the electronic population in the inorganic (organic) side of the interface (see Figure 7, right panel).
4 Conclusions and Outlook

To summarize, in the first-principles framework of RT-TDDFT, we have investigated the laser-driven charge-carrier dynamics of a two-dimensional hybrid inorganic/organic heterostructure formed by a MoSe$_2$ monolayer and physisorbed pyrene molecules. By impinging the system with a femtosecond pulse in resonance with the HOMO→LUMO transition of the molecule and with intensities ranging from 200 to 5000 GW/cm$^2$, we find a pronounced intensity-dependent response, which manifests itself in high-harmonic generation, in the nonlinear behavior of the excitation energy and of the number of excited electrons, and, most interestingly, in the inversion of the photo-induced charge-transfer direction with respect to the linear regime. This behavior is ascribed to Pauli blocking: saturated absorption from occupied pyrene-like states to unoccupied MoSe$_2$ bands inhibits charge transfer from the molecule to the monolayer, while promoting the same process in reverse.

The presented study represents a proof of concept for laser-controlled charge transfer in molecularly doped TMDCs, paving appealing routes for exploiting these hybrid materials for quantum-optoelectronic applications such as ultrafast optical switches. The proposed analysis is expected to be complemented by future work including thermal effects and dissipation mechanisms induced, above all, by phonons. While the former can impact on the level alignment predicted at 0K, electron-vibrational interactions are expected to become crucial on timescales on the order of picoseconds or higher, i.e., well above the femtosecond range of coherent electronic response the laser excitation, which is the key responsible for the effects discussed in this work.
5 Methods

5.1 Theoretical Background

The results presented in this work are obtained in the framework of density functional theory (DFT)\textsuperscript{57} and RT-TDDFT.\textsuperscript{48} In the former, the task of solving the Kohn-Sham (KS) equations\textsuperscript{49} is performed in a time-independent framework, while the explicit time-dependence of the electron density is considered in the latter.

DFT calculations offer access to (a qualitative picture of) the electronic structure of materials. When hybrid systems are considered, the so-called supercell approach is typically adopted. As in this case, the reciprocal lattice vectors are sub-multiples of those of the reference unit cell, an intuitive interpretation of the band-structure plot is often inhibited. To overcome this problem, band-unfolding techniques have been developed\textsuperscript{50–52} in order to map the results obtained in the supercell into the Brillouin zone of the reference unit cell. Following the approach presented in Ref. 31, this is done by introducing the spectral function

$$W(k, E) = \sum_{n, g} |c_{nK}(G_0 + g)|^2 \delta(E - E_n(K)),$$

where the sum runs over all bands $n$ and the primitive-cell reciprocal lattice (represented by $g$), $E_n(K)$ is the band energy, and $k = K + G_0$, \textit{i.e.} $k$ (in the primitive-cell Brillouin zone) folds into $K$ (in the supercell Brillouin zone) with the supercell reciprocal lattice vector $G_0$. In Eq. (1), $c_{nK}(G)$ are the plane-wave coefficients of the Bloch functions

$$\phi_{nk}(r) = e^{ikr} \sum_G c_{nk}(G)e^{iG\cdot r},$$

where $G$ are the supercell reciprocal lattice vectors.

In the performed RT-TDDFT calculations, the time-dependent KS equations are solved within the adiabatic approximation of the exchange-correlation functional with the explicit
inclusion of an electric field of the form (the velocity-gauge is assumed hereafter):

\[ E(t) = -\frac{1}{c} \frac{dA(t)}{dt}. \]  

(3)

In this way, the Schrödinger-like equation reads

\[ i \frac{\partial \phi_{nk}(r, t)}{\partial t} = \left( \frac{1}{2} \left( -i \nabla + \frac{A(t)}{c} \right)^2 - \sum_i \frac{Z_i}{|R_i - r|} + \int d^3r' \frac{n(r', t)}{|r - r'|} + v_{xc}[n(r, t)] \right) \phi_{nk}(r, t), \]

(4)

where \( \phi_{nk}(r, t) \) and \( n(r, t) \) are the time-dependent KS orbitals and electron density, respectively, \( Z_i \) and \( R_i \) are the nuclear charges and positions, respectively, and \( v_{xc} \) is the exchange-correlation potential. The solutions of Eq. (4) give access to the time-dependent electronic properties of the system. While this method has established itself in the realm of molecules and non-periodic systems, where many-body correlations not captured by the mean-field TDDFT approach are often negligible,\(^{53,54}\) extensions of the formalism have made it capable to treat crystalline materials as well.\(^{29,55–58}\)

With the computed \( \phi_{nk}(r, t) \), one can obtain the time-dependent macroscopic current density as

\[ J(t) = \int_{\Omega} d^3r \frac{1}{2} \sum_{nk} \left[ \phi_{nk}^*(r, t) \left( -i \nabla + \frac{A(t)}{c} \right) \phi_{nk}(r, t) + c.c. \right], \]

(5)

where the integration is performed in the unit cell with volume \( \Omega \). The high harmonic spectrum of this quantity,\(^{55}\)

\[ J(\omega) = \left| \int dt \ \partial_t J(t) e^{-i\omega t} \right|^2, \]

(6)

can be used to probe high-harmonic generation.

The number of excited electrons during the laser-induced electron dynamics of the system
is calculated as
\[
N_{\text{ex}}(t) = N_{\text{tot}} - \sum_{n,n',k} P_{n',k}(t)\langle \phi_{n,k}(t=0) | \phi_{n',k}(t) \rangle^2,
\]
where \( P_{n',k}(t) \) is the population of \( n' \)-th state at \( k \) and time \( t \). The occupation density is calculated by weighting the density of states with the projection of the occupied time-dependent KS states into the ground-state ones at a certain time \( t \):
\[
\mathcal{N}(\epsilon,t) = \sum_{n',n,k} \sum_{\text{all}} P_{n',k}(t) \delta(\epsilon - \epsilon_{nk}^0) \langle \phi_{n,k}(t=0) | \phi_{n',k}(t) \rangle^2.
\]

### 5.2 Computational Details

All calculations presented in this work are performed using the real-space grid code OCTO-PUS, with the exception of the band structure, as discussed below. For the approximation of the exchange-correlation functional, we adopt the adiabatic local density approximation (ALDA), and for treat core electrons we use the Hartwigsen-Goedecker-Hutter (HGH) LDA pseudopotentials. The calculations were done using a cubic grid with a spacing of 0.2 Å, a 3x3x1 k-grid in the super cell approach with a Coulomb cutoff of 20 Å applied in the z-direction. The time-dependent electric fields are modelled as an \( x \)-polarized and Gaussian-envelope pulse, centered at \( t_\mu = 12 \) fs with standard deviation \( t_\sigma = 2 \) fs and a carrier frequency of \( \omega_0 = 3.1 \) eV. Simulations for different intensities (\( I \)) have been carried out using the approximated enforced time-reversal symmetry propagator with a time step of 2.42 as and total propagation time of 30 fs. For the time-dependent Bader charge analysis, the time-dependent density was printed at every 0.35 fs and the charge for the TMDC and pyrene was calculated then summit the individual charges of each atoms. The time-dependent Bader charges shown in Figure are fit with an 11-th degree Polynomial model for Support Vector Regression, using the scikit-learn package.

The calculation of the band structure shown in Figure (b) is performed with version 6.7
of the Quantum Espresso suite,\textsuperscript{64,65} using norm-conserving and scalar-relativistic PZ-LDA pseudopotentials generated with the Ape code.\textsuperscript{66} We use plane-wave cutoffs of 40 Ry and 160 Ry for the wavefunctions and the density, respectively. The density of states is calculated on a $100 \times 100 \times 1$ $k$-grid by Wannier interpolation, using the Wannier90 code.\textsuperscript{67} A broadening of 25 meV is applied. The contributions from pyrene are determined by projection onto the molecule-centered Wannier functions.

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**Supporting Information Available**

In the Supporting Information, we report the linear absorption spectra of the pyrene/MoSe$_2$ hybrid interface as well as the analysis of the lowest excited states in gas-phase pyrene. We also include the time evolution of excitation energy and number of excited electrons for additional laser intensities together with the charge density difference maps at varying pulse intensity. Refs. \textsuperscript{68} \textsuperscript{74} are cited therein.
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