Mode-selective exciton-phonon dynamics in MoS$_2$

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Two-dimensional crystals of transition metal dichalcogenides are emerging as promising candidates for next-generation optoelectronic and quantum devices. In such systems, the interaction between excitonic states and atomic vibrations is crucial for many fundamental properties, such as carrier mobilities, quantum coherence loss, and heat dissipation. In particular, to fully exploit their valley-selective excitations one has to understand the many-body exciton physics of zone-edge states. So far, theoretical and experimental studies have mainly focused on the exciton-phonon dynamics in high-energy direct excitons involving zone-center phonons. Here, we use ultrafast electron diffraction to investigate the structural dynamics occurring during nearly-resonant excitation of low-energy indirect excitons in MoS$_2$. By exploiting the large momentum carried by scattered electrons, we identify the selective excitation of in-plane K-phonon modes with $E_{2g}^1$ and $E_{1u}$ symmetry. Our results highlight the strong selectivity of phononic excitations directly associated with the specific indirect-exciton nature of the wavelength-dependent electronic transitions triggered in the system.

The understanding and active control of nanoscale materials are crucial for addressing the technological challenges of the 21st century, associated with the demands for data processing, storage, and transmission. In such a context, transition metal dichalcogenides (TMDCs) are showing great promises to satisfy these demands due to their unique physical properties [1], resulting from a subtle balance between electronic, lattice, and valley degrees of freedom [2,3]. The ability to shift such balance would provide a promising way to manipulate their behavior, thus offering unprecedented opportunities for optoelectronics as well as quantum technologies.

In equilibrium conditions, the system mainly explores thermodynamically stable states described within the Ehrenfest’s scheme. Instead, perturbing the free-energy landscape using femtoseconds (fs) electromagnetic fields can lead the system toward transient states that are not accessible under equilibrium ergodic conditions [4]. Controlling these states and dynamically
engineering their appearance on a microscopic level would allow to manipulate the macroscopic functionality of the system. This is particularly relevant for many-body exciton physics that exploits the valley-selectivity typical of TMDCs [5,6,7], with a profound technological impact on the design of next-generation gates, memories, photon emitters as well as thermoelectric devices.

In the non-equilibrium regime, the Born-Oppenheimer approximation fails to describe the state of the system, and interactions between electronic and atomic degrees of freedom have a crucial role in determining their fundamental properties, such as electron mobility [8], quantum coherence loss, and dephasing [9,10], heat generation and dissipation [11]. A complete understanding is thus only obtained when capturing such electronic-driven structural dynamics at the proper length (atomic) and temporal (femtosecond) scales.

Here, we adopted ultrafast electron diffraction (UED) to investigate the exciton-phonon dynamics in nano-flakes of molybdenum disulfide (MoS2), the prototypical TMDC. Following nearly-resonant excitation of low-energy indirect excitons at the K point of the Brillouin zone, we observed selective excitation of in-plane K-phonon modes with $E_{1g}^2$ and $E_{1u}$ symmetry. Our observations complete previous studies of exciton-phonon dynamics in MoS2 that reported strong coupling of direct excitons with out-of-plane $A_{1g}$ Γ-phonons [5,6]. The direct investigation of atomic motions in real-time has become possible only recently thanks to the development of highly-sensitive ultrafast electron and X-ray diffraction techniques [12,13,14,15,16]. By exploiting the large momentum carried by diffracted electrons, UED allows to explore short-range and long-range atomic-scale motions of the lattice [17,18,19,20,21,22,23,24], as well as zone-edge atomic vibrations that are not detectable with the usually adopted optically-based techniques, which are instead only sensitive to zone-center phonons because of the small momentum of light.

Nano-flakes of single-crystals MoS2 were obtained via mechanical exfoliation from a natural MoS2 bulk crystal, and then transferred onto a TEM Cu grid. The schematic of the UED experiment is shown in Fig. 1a: ultrashort electron pulses are focused in normal incidence on the MoS2 flake. The dynamics is initiated by ultrashort laser pulses with a variable wavelength (either 800 nm or 400 nm), temporal duration of 120 fs, repetition rate of 2 kHz, and with a fluence of 11.8 mJ/cm$^2$ or 5.9 mJ/cm$^2$ for the two wavelengths, respectively. The diffracted electrons are then recorded on a CCD detector in the stroboscopic mode at different delay times between the excitation laser and the probing electron pulse. Further details on the sample preparation and experimental setup are given in the Methods section.

MoS2 is probably the most studied member of the transition metal dichalcogenide family. It is characterized by S-Mo-S single layers bonded together by weak van der Waals interactions. Each layer consists of two hexagonal planes of S atoms intercalated by one hexagonal plane of Mo atoms. Molybdenum is bound with Sulfur via a trigonal prismatic arrangement (space group is P3m1 and point group is D$_{6h}$). Fig. 1b shows a representative diffraction pattern measured before laser excitation, showing the in-plane hexagonal pattern typical of a D$_{6h}$ crystal where we can identify three high-symmetry lattice plane families: {1100}, {0110}, and {1010}.

MoS2 in its bulk form is an indirect semiconductor with a bandgap of 1.29 eV along the Γ-K direction of the Brillouin zone (see Fig. 1c). The direct gaps in Γ and in K are, instead, on the order of 3 eV. This means that optical excitation at 400 nm (3.1 eV) can induce strong vertical interband electronic transitions across almost the entire Brillouin zone (see blue arrows in Fig. 1c) with no momentum change required for the electron. Instead, in the case of optical excitation at 800 nm (1.55 eV), the only allowed transitions would be non-vertical interband electronic transitions
mediated by the presence of a phonon necessary to fulfill the momentum conservation (see red arrows in Fig. 1c). Such wavelength-dependent physics thus gives us an unprecedented opportunity to dynamically investigate the coupling between electronic and phononic degrees of freedom in a 2D material.

A direct consequence of such an effect is the formation of indirect excitons following the 800 nm optical excitation. In multi-layers MoS$_2$, photoluminescence (PL) spectroscopy has evidenced the presence of a well-defined feature in the range 1.4 – 1.6 eV [25], which was associated with indirect radiative recombination processes. In the bulk 2H-MoS$_2$, momentum-resolved electron energy-loss spectroscopy measurements have observed a strong excitation dispersing from 1.46 eV to 1.57 eV along the Γ-K direction [26] for a momentum value of the order of $q_K = 1.33$ Å$^{-1}$, which corresponds to the momentum-space difference between the Γ and the K points of the Brillouin zone. The authors thus attributed such feature to an indirect $\Gamma_V$-$K_C$ exciton (where the suffix V and C stand for valence and conduction, respectively). Considering the $\Gamma$-$K$ energy gap to be around 1.29 eV, this corresponds to an exciton binding energy between 280 meV and 170 meV.

In our experimental configuration, we used laser light at 800 nm (1.55 eV) to induce a nearly-resonant excitation of such indirect $\Gamma_V$-$K_C$ excitons, while light at 400 nm (3.1 eV) would mainly promote the formation of hot carriers around the Γ and K points without momentum transfer. As we will show below, the different nature of the transient electronic excitation would directly influence the coupling to the phononic subsystem and lead to completely different scenarios in terms of structural dynamics.

In Fig. 2 we show the measured diffraction intensity changes recorded as a function of the delay time between the optical pump and the electron probe for the three high-symmetry directions evidenced in the diffraction pattern in Fig. 1b when using light at 800 nm (Fig. 2a-c) and at 400 nm (Fig. 2d-f). The transient change of the Bragg reflections unveils the non-equilibrium lattice dynamics. In the kinematic theory, the diffraction intensity of a given Bragg peak, $I_{[hkl]}$, is determined by the square modulus of the structure factor, $F_{[hkl]}$, which depends on the atomic displacement with respect to the equilibrium positions:

$$F_{[hkl]} = \sum_j \xi_j \exp \left[ i \mathbf{s}_{[hkl]} \cdot (\mathbf{R}_j + \mathbf{u}_j(t)) \right]$$

Here, $\mathbf{u}_j$ defines the displacement of the j-th atom within the unit cell with respect to the equilibrium position $\mathbf{R}_j$, and $\xi_j$ is the atomic scattering factor. Atomic vibrations associated with optical and acoustic phonons will induce a net nonuniform displacement within the lattice, resulting in a modification of the structure factor, and thus a transient variation of the diffraction intensity. A positive or negative change of the diffraction intensity would thus correspond to the excitation of specific vibrational modes able to induce a positive or negative change, respectively, of the structure factor for the given Bragg reflection.

In the case of optical excitation at 400 nm (3.1 eV), the observed transient intensity change exhibits a progressive drop for all measured diffraction peaks with a time constant on the order of a few tens of picoseconds. This behavior is characteristic of semiconducting systems following above band-gap excitation, where a large population of hot carriers is produced. The hot carriers cool down via direct coupling to hot optical phonons, which in turn anharmonically decay toward long-wavelength acoustic phonons. The increased dynamic disorder induced by the large-
amplitude low-energy acoustic vibrations will consequently create a non-negligible loss of electron interference responsible for the decrease of diffraction intensity.

In the case of optical excitation at 800 nm (1.55 eV), the observed behavior is different. Here, while the \{1\text{\textbar}00\} Bragg peak still exhibits an intensity drop, the peaks associated with the \{0\text{\textbar}1\text{\textbar}0\} and \{10\text{\textbar}0\} reflections show, instead, a sharp intensity increase on a time scale of a few picoseconds (4–5 ps) before recovering toward a negative change on a longer time scale of tens of picoseconds. Such early-time behavior indicates a positive increase of the structure factor, which is characteristic of a situation where only a subset of phonons is excited within the lattice, as observed – for instance – in the case of infrared resonant excitation of selective vibrational modes in strongly-correlated electron materials [27]. This is consistent with the nature of the electronic excitation at 1.55 eV, where indirect \Gamma\text{\textbar}K_C excitons are stabilized via the excitation of a subset of phonons with a well-defined momentum.

To quantitatively elucidate the transient atomic behavior of the lattice following the electronic excitation, we have calculated via density functional theory (DFT) the atomic details of the 18 normal vibrational modes allowed for a 2H-MoS\textsubscript{2} bulk crystal (further details on the DFT calculations are given in the Methods section). Fig. 3a shows the calculated phonon dispersion, while Fig. 3b-g report the modulation of the square modulus of the structure factor, $|F_{hk\ell}|^2$, calculated for each vibrational mode. For our analysis we have considered phonon modes at the \Gamma point (Fig. 3e-g) and K point (Fig. 3b-d) of the Brillouin zone, and calculated the structure factor for the three Bragg reflections monitored in this study.

From the calculations we can immediately notice that in the case of excitation of \Gamma phonons, the structure factor change is always negative. This is consistent with the experimentally measured decrease of the diffraction intensity for illumination at 400 nm, which results in the vertical excitation of hot carriers with zero transferred momentum and thus in the generation of optical and acoustic phonons at the \Gamma point.

Different is the situation in the case of excitation of phonon modes at the K point. Here, we found that not all phonons contributed to a negative modulation of the structure factor. For the \{10\text{\textbar}1\} reflection the $E_{1g}^3(K)$ mode at 45.9 meV (370 cm$^{-1}$) gives a strong positive contribution, while for the \{01\text{\textbar}0\} reflection there are actually two modes, the $E_{2g}^1(K)$ and the $E_{1u}(K)$ at 41.3 meV (333 cm$^{-1}$), which contribute to the positive modulation. This behavior is perfectly consistent with the measured transient intensity increase for the \{10\text{\textbar}1\} and \{01\text{\textbar}1\} reflections following illumination at 800 nm. Here, the nearly-resonant excitation of indirect \Gamma\text{\textbar}K_C excitons would induce the stabilization of a subset of phonons with a well-defined momentum $q = K$.

By comparing the calculated structure factor changes in Fig. 3 with the experimental results in Fig. 2, we can now identify the microscopic nature and symmetry of the involved lattice vibrations coupling to the indirect excitons at $\sim 1.5$ eV, which are mainly determined by the $E_{2g}^1(K)$ and the $E_{1u}(K)$ in-plane modes of the MoS\textsubscript{2} lattice. Fig. 3h-j shows the direction of atomic motion within the unit cell for the two modes, which evolves in the $ab$ plane along the diagonals of the unit cell base, while in the Supplementary Movies 1 and 2 the reader can visually observe the temporal sequence of their motion.

By directly unraveling the structural origin behind the indirect excitations in MoS\textsubscript{2}, our observations complete previous theoretical and experimental investigations of exciton-phonon
dynamics in MoS2 that only explored direct excitons. In particular, these works reported strong coupling of the A and B direct excitons at ~1.85 eV and ~2.1 eV, respectively, with $A_{1g} (\Gamma)$ out-of-plane phonon modes [5,6]. More interestingly, in these works, it was observed that when the exciton wave function has contributions from different parts of the momentum space, such as in the case of high-energy C excitons at 2.7 eV, the favored coupling occurs with $E_{2g}^1$ modes, in line with our findings for indirect excitons.

Moreover, the fact that excitons mainly couple to high energy optical phonon modes is consistent with the calculated Eliashberg function in MoS$_2$, which shows higher electron-phonon coupling probabilities in the high-frequency range [28,29]. Our results are also consistent with recent investigations of electron-phonon interaction in MoS$_2$ via ultrafast visible/IR spectroscopy, where the authors observed the appearance of a well-defined feature in the frequency range 380-390 cm$^{-1}$ following excitation at 800 nm [30], which they attribute to the excitation of in-plane phonon modes with $E_{1u}$ symmetry.

Such mode-selective phonon excitation observed for illumination at 800 nm is directly associated with the specific indirect-exciton nature of the wavelength-dependent electronic transition triggered in the system. Therefore, given the indirect character of such electronic states, we expect that the coherent structural response of the lattice would persist over long time scales. The preservation of such structural coherence can be directly seen by monitoring the transient change of the interatomic distance, shown in Fig. 4 for the case of the $[0\overline{1}10]$ direction. We observed the presence of in-plane breathing oscillations with a frequency of 72.9 GHz – corresponding to a period of 13.7 ps. This is consistent with experimentally reported in-plane strain waves in MoS$_2$ nano-flakes observed at a frequency of about 50 GHz [31,32]. This coherent lattice oscillation can be seen as the result of an anharmonic coupling of the excited high-energy $E_{2g}^1(K)$ and $E_{1u}(K)$ in-plane phonon modes to low-energy acoustic vibrations [33] that will quickly relax into low-frequency in-plane strain waves.

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METHODS

Preparation of MoS$_2$ nano-flakes

MoS$_2$ nano-flakes used here are mechanically exfoliated from a 100% natural MoS$_2$ crystal provided by SPI Supplies/Structure Probe, Inc.. In detail, we use scotch tape to exfoliate thin flakes off the bulk MoS$_2$ after numerous repetitions, and then immerse the tape with MoS$_2$ flakes in acetone. After 3 - 4 minutes, we shake the tape in the acetone to detach MoS$_2$ flakes and then fish them by using 200-mesh Cu TEM grids. Here, we visually pick up half-transparent or nearly transparent MoS$_2$ flakes as the sample. To remove the acetone, we rinse the TEM grid with MoS$_2$ many times by using deionized water. Finally, the grids are dried in the air for UED measurements.

Ultrafast electron diffraction (UED)

For the UED measurements, the output of a Ti:Sapphire regenerative amplifier ($\lambda = 800$ nm, 100 fs, 2 kHz) was separated in two portions: one represents the optical pump beam that is responsible for exciting the sample; the other was used to generate ultraviolet pulses by third-harmonic generation ($\lambda = 266$ nm), which irradiate a LaB$_6$ photocathode to produce ultrafast electron pulses. The diffraction patterns generated by electron scattering from the samples were recorded in far-field on a gated CCD detector and monitored as a function of the delay time between pump and probe. For the investigation of MoS$_2$ nanoflakes, we adopted a normal incidence geometry (transmission scheme), tracking the transient behavior of the in-plane reflections.

To minimize space charge effects, an electron pulse was designed to contain less than 300 electrons, giving a sub-ps pulse duration. Particular care was taken for the calibration of the zero-delay time, i.e. the time at which the electron and laser pulses simultaneously arrived on the sample. We used multiphoton ionization from a metallic surface, which created a transient and localized plasma synchronous with the laser excitation able to modify the electron pulse’s position and spatial profile (“plasma lensing effect”). Finally, we note that within the adopted fluence range transient electric field effects on the measured diffraction pattern were negligible and did not affect the measured dynamics [34].

DFT calculations of phonon band structure

Band structure calculations are carried out with the Vienna Ab-initio Simulation Package (VASP) [35] based on the Density Functional Theory with projector-augmented-wave (PAW) [36,37] pseudopotentials. The generalized gradient approximation (GGA) with the Perdew-Burke-Enzerhof (PBE) parametrization is used for the exchange and correlation functional [38]. The computations are based on a unit cell consisting of 6 atoms with an 8×8×8 k-point mesh along the path Γ-K within Monkhorst-Pack scheme and cutoff energy of 500 eV. The convergence criteria for total energies and forces are $10^{-8}$ eV and $10^{-6}$ eV/Å, respectively. The bulk geometry used to simulate MoS$_2$ has a relaxed lattice parameter of $a = 3.18$ Å, $b = 3.18$ Å, $c = 13.13$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$.

The phonon dispersion is calculated using the direct force-constant method implemented in the PHONOPY code [39]. In this method, a specific atom is displaced to calculate the induced
Hellmann Feynman forces on itself and its surrounding atoms. By collecting the Hellmann Feynman forces one can construct the dynamical matrices that lead to the phonon properties and thermodynamic functions within the framework of lattice dynamics and harmonic approximation. Because of the effects of image atoms due to the periodic boundary conditions, larger supercell is needed to make sure all calculated phonon frequencies are well converged. We employed a 4×4×2 supercell with 192 atoms for phonon calculations which are well converged in this work.
Figure 1. UED experiment on nano-flakes of MoS$_2$. (a) Schematic representation of the UED experiment where ultrashort electron pulses are focused in normal incidence on the MoS$_2$ flake and the dynamics is initiated by ultrafast laser pulses with a variable wavelength (either 800 nm or 400 nm). The diffracted electrons are then recorded in stroboscopic mode at different delay times between the excitation laser and the probing electron pulse. (b) Representative diffraction pattern measured before laser excitation, showing the in-plane hexagonal pattern typical of a D$_{6h}$ crystal where we can identify three high-symmetry lattice plane families: $\{11\bar{0}0\}$, $\{01\bar{1}0\}$, and $\{10\bar{1}0\}$. (c) Schematic representation of the electronic band structure for a 2H-MoS$_2$ bulk crystal showing an indirect band gap of 1.29 eV along the $\Gamma$-K direction of the Brillouin zone; the direct gaps in $\Gamma$ and in K are, instead, on the order of 3 eV. The blue and red arrows represent allowed transitions following optical excitations at 400 nm (3.1 eV) and 800 nm (1.55 eV), respectively.
Figure 2. Transient lattice evolution following the optical excitation. The measured diffraction intensity changes are recorded as a function of the delay time between the optical pump and the electron probe for the three high-symmetry directions evidenced in the diffraction pattern in Figure 1b when using light at 800 nm and at 400 nm. (a) \{10\overline{1}0\} reflection at 800 nm; (b) \{01\overline{1}0\} reflection at 800 nm; (c) \{1\overline{1}00\} reflection at 800 nm; (d) \{10\overline{1}0\} reflection at 400 nm; (e) \{01\overline{1}0\} reflection at 400 nm; (f) \{1\overline{1}00\} reflection at 400 nm.
Figure 3. DFT calculations of phonon modes and structure factor changes. Density Functional Theory (DFT) calculations of the normal vibrational modes for a 2H-MoS$_2$ bulk crystal. (a) Calculated phononic band structure along the $\Gamma$-K direction of the Brillouin zone. (b)-(d) Calculated modulation of the square modulus of the structure factor, $|F_{hkl}|^2$, obtained for each vibrational mode in the $\Gamma$ point with respect to the equilibrium static configuration. (e)-(g) Calculated modulation of the square modulus of the structure factor, $|F_{hkl}|^2$, obtained for each vibrational mode in the K point with respect to the equilibrium static configuration. (h), (j)
Representation of the direction of atomic motion within the unit cell for the $E_{2g}^1(K)$ and the $E_{1u}(K)$ in-plane modes of the MoS$_2$ lattice, evolving within the $ab$ plane along the diagonals of the unit cell base.

Figure 4. Long-term coherent lattice dynamics. Transient change of the interatomic distance measured for the case of the [0\overline{1}10] direction, showing in-plane breathing oscillations with a frequency of 72.9 GHz (period of 13.7 ps). This behavior is consistent with a coherent structural response of the lattice persisting over long time scales.
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