

Intervalley scattering in monolayer MoS₂ probed by non-equilibrium optical techniques

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ABSTRACT

Here we study the exciton valley relaxation dynamics in atomically thin MoS₂ by non equilibrium optical techniques. A spin polarized excitons population is selectively created in a single valley by circularly polarized ultrashort laser pulses resonant with the optical gap, while the subsequent decay of the valley polarization is measured as a rotation of a linearly polarized probe beam due to a transient Faraday effect. We show that the photoinduced valley polarization in monolayer MoS₂ is quenched after few ps due to an efficient intervalley scattering channel and it displays a peculiar bi-exponential behavior. This rapid time scale is in a good agreement with an intervalley scattering mechanism mediated by an electron-hole exchange interaction. Moreover time resolved circular dichroism experiments performed in the same experimental condition confirms the fast valley relaxation dynamics observed with transient Faraday rotation technique.

1. INTRODUCTION

Valleytronics aims at the exploitation of the additional degree of freedom emerging in materials where the energy of the carriers may assume several equal minimum values (valleys) at non-equivalent points of the reciprocal space¹. In this context, single layers of transition metal dichalcogenides (TMDs) have very promising characteristics^{2,3}.

In single layer MoS₂ the minimum of the conduction band is located at the corners K and K' of the hexagonal Brillouin zone (Fig.1), providing two non-equivalent direct bandgaps in the visible range ($\lambda_{gap}=655$ nm at room temperature). In the valence band the lack of inversion symmetry and the strong spin-orbit interaction remove the energy degeneration between the two electronic states, resulting in a valence band spin splitting $\Delta E_{SO} = 160$ meV. The electronic states on the top of the valence band at the K valley are linear superposition between transition metal (TM) d orbitals characterized by the orbital quantum number $l=2$ and a projection along the quantization axis $m_l=2$ and a small contribution coming from the p orbitals of the chalcogen (C) atom ($l=1$, $m_l=+1$). These states are schematically described by the notation $\alpha |TM, l=2, m_l=2\rangle + \beta |C, l=1, m_l=1\rangle$ for the orbital part and the spin wave function $|\uparrow\rangle, |\downarrow\rangle$ (projection of the spin quantum number $m_s=\pm 1/2$) respectively for the lower and higher energy valence band states^{4,5}. Furthermore time reversal symmetry requires that the electronic states at the top of K and K' are complex conjugated and the valence band spin splitting has opposite sign in the two valleys. The electronic states at the bottom of the conduction band are

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constructed by a linear superposition of d TM orbital characterized by $m_l=0$ and the p orbital of the C atom ($\alpha' |TM, l = 2, m_l = 0\rangle + \beta' |C, l = 1, m_l = -1\rangle$). For the sake of simplicity the electronic states are labeled with the projection of their average angular momentum $\langle L_z \rangle$ along the direction perpendicular to the MoS₂ plane (see Fig.1, left panel). Conversely to the valence band, the conduction band spin orbit splitting is of the order of few meV and the electronic states $|\uparrow\rangle, |\downarrow\rangle$ can be considered as degenerate. The electronic state in K' are the time-reversed of the electronic state in K.

Given the large spin-orbit interaction acting on the valence band of monolayer MoS₂, optical orientation represents a unique tool to inject high spin and valley polarizations for both electrons and holes. In this process, dipole selection rules for optical transitions with circularly polarized light allow the excitation of an electron/hole population in the conduction/valence band with a net spin polarization $P = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$, where $n_{\uparrow(\downarrow)}$ are the up (down) spin densities (as referred to a proper quantization axis). At variance from optical orientation in common bulk semiconductors, in single layer MoS₂ the left (right)-circularly polarized light promotes spin oriented electrons at the bottom of the conduction band only at the K (K') point of the Brillouin zone due to the valley selectivity, thus reaching a potential initial spin polarizations up to 100%^{2,7-9} and enabling the optical control of the electron momentum, which can be exploited to observe the so-called valley Hall effect¹⁰.

The MoS₂ optical absorbance in the visible range is characterized by two peaks centered about 1.9 eV and 2.05 eV (denoted as A and B). The physical origin of these peaks is attributed to band-edge optical transition from the top of the spin splitted valence band to the bottom of the conduction band⁶. These optical transitions are strongly renormalized by excitonic effects which are enhanced by the 2D structure of the material.

At the present several theoretical and experimental works have been dedicated to the study of the valley dynamics in MoS₂ and other one dimensional transition metal dichalcogenides with controversial results. Although from early helicity-resolved photoluminescence (PL) measurements an exciton valley/spin lifetime of the order of ~ 1 ns was inferred⁷, recent time resolved PL¹¹ and helicity resolved pump probe measurements^{12,13} clearly show that the valley polarization is quenched after few ps.

In this paper we measure the exciton valley relaxation dynamics in a MoS₂ monolayer by Time Resolved Faraday Rotation (TRFR)¹⁴. The photoinduced valley polarization exhibits two distinct decay rates and it is quenched after few ps. This result entails a quick scattering of the photoexcited spin polarized excitons from the valley K to K'. The slower decay dynamics of ~ 5 ps is interpreted as a residual component of the valley polarization, in agreement with the results obtained by polarization resolved transient transmittivity measurements¹². The fast valley polarization decay time can be explained in term of an electron-hole exchange interaction mechanism (Maialle-Silva-Sham mechanism)^{15,16}. We further investigate the valley depolarization dynamics in monolayer MoS₂ by time resolved circular dichroism experiments (TRCD). Due to the reduced screening of the Coulomb interaction, the electron-hole pairs, selectively excited in one valley by circularly polarized pulses, are scattered very rapidly in the opposite valley. The resulting valley depolarization dynamics, measured with TRCD, displays the same relaxation pathway of the one measured by TRFR.

2. EXPERIMENTAL SETUP AND SAMPLE CHARACTERIZATION

A regenerative amplified mode locked Ti:Sapphire laser (Clark-MXR model CPA-1) providing 150 fs and 500 μ J light pulses, at a central frequency of 780 nm and repetition rate of 1 kHz drives two non collinear optical parametric amplifiers (NOPA). The output of the first NOPA, used to inject spin polarized carriers in the sample, is tuned to 650 nm, i.e. quasi resonant to the A exciton, and it is circularly polarized by passing through a quarter wave plate. The probe pulse, provided by the second NOPA, is linearly polarized and it is centered at a frequency of 700 nm. Both pump and probe pulses has a spectral bandwidth of 10 nm. The temporal delay between the two pulses is adjusted by a mechanical delay stage. The transmitted probe pulse passes through a Wollaston prism and it is focused on a couple of balanced photodiode. The Wollaston prism is rotated in order to balance the probe intensities on the two photodiodes. The pump induced imbalance of the signal measured by the two photodiodes is registered by a lock-in amplifier which is locked to the modulation frequency of the pump beam (i.e. 500 Hz).

In the TRCD experiment the pump beam is generated by a NOPA at a frequency of 650 nm and it is circularly polarized. The probe is a white light pulse, ranging between 500 nm and 700 nm, generated by focusing the fundamental pulse in a 1 mm sapphire plate. The probe pulse is circularly polarized by a broadband quarter wave plate. A fast analogue-to-digital conversion card with 16-bit resolution enables single-shot recording of

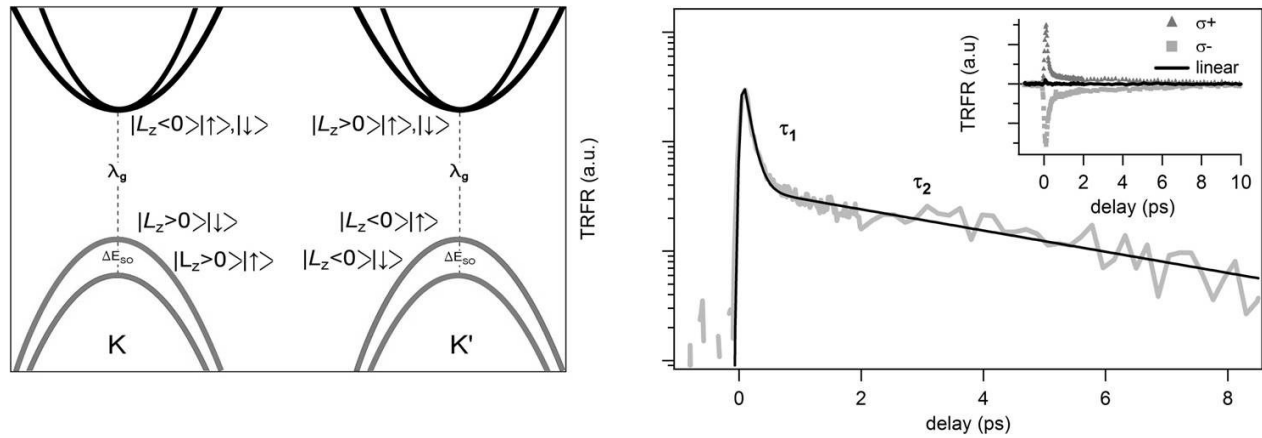


Figure 1. Left panel: 1L-MoS₂ band structure around K and K'. The electronic states are labeled as a function of the projection of their average angular momentum along the direction perpendicular to the plane and the spin angular momentum. Right panel: time resolved Faraday rotation signal measured at 77 K. The pump pulse is circularly polarized and its wavelength is resonant with the A exciton transition (i.e 650 nm) while the probe wavelength is tuned below the optical bandgap (i.e. 700 nm). The black curve is a double exponential decay function convoluted with a gaussian pulse accounting for the temporal resolution of the experiment. In the inset, TRFR traces measured by exciting the sample with left and right circularly polarized pump pulses (triangles and squares, respectively) and a linearly polarized pump pulse (continuous line). The signal of TRFR dynamics measured with opposite pump polarization is reversed because of the MoS₂ valley selective circular dichroism. The TRFR signal resulting by pumping with linear polarized light is zero because the two valleys in K and K' are equally populated.

the probe spectrum at the full 1-kHz repetition rate. The two dimensional maps $\Delta T/T$, reported in Fig.2, are obtained by recording the transmitted spectra with and without the pump excitation at different delay times. MoS₂ flake are obtained by micromechanical cleavage of bulk MoS₂ crystals on a Si-SiO₂ substrate, identified by optical contrast and characterized by Raman and PL spectroscopy. The sample is then transferred onto a fused silica substrate by a wet-transfer technique based on a sacrificial layer of poly-methyl-methacrylate (PMMA)^{17,18}. In order to check if the integrity of the MoS₂ flake is preserved the sample is further characterized after the transfer¹⁴.

3. VALLEY RELAXATION DYNAMICS IN MONOLAYER MOS₂

In Fig.1 (right panel) the Time Resolved Faraday Rotation (TRFR) signal on a single layer MoS₂ at 77 K is reported. The laser excitation wavelength is set to 650 nm, i.e. resonant with the lower excitonic transition identified by photoluminescence measurements. Since the interband optical transitions in 2D TMDs are governed by helicity dependent selection rules, the circularly polarized pump beam creates a spin polarized electron-hole pair in one of the two non equivalent valleys. The probe wavelength is tuned below the optical gap (i.e. 700 nm). In this non degenerate configuration, the Faraday rotation is not sensitive to the spin relaxation processes occurring within the same valley and it directly probes the valley depolarization dynamics due to the intervalley scattering processes.

The TRFR signal relaxes with two different timescales, dropping to 10% of the initial value after few hundreds of fs. The decay times are extracted by fitting the temporal trace with a double exponential decay function convoluted with a gaussian pulse accounting for the experimental resolution (i.e. 70 fs). The faster dynamics τ_1 is 200 fs while the slower one τ_2 is about 5 ps. We identify this rapid drop of the Faraday signal as a result of the intervalley scattering of the photoexcited carriers. A possible mechanism compatible with such a rapid decrease of the valley polarization, is due to the electron-hole exchange Coulomb interaction¹⁵. This process can be described as a virtual annihilation of a bright exciton in one valley followed by a creation of an exciton in the opposite valley. Since the time scale associated to this process is on the order of the inverse of the Coulomb interaction energy scale, the decrease of the valley polarization is expected to be extremely fast. The temporal

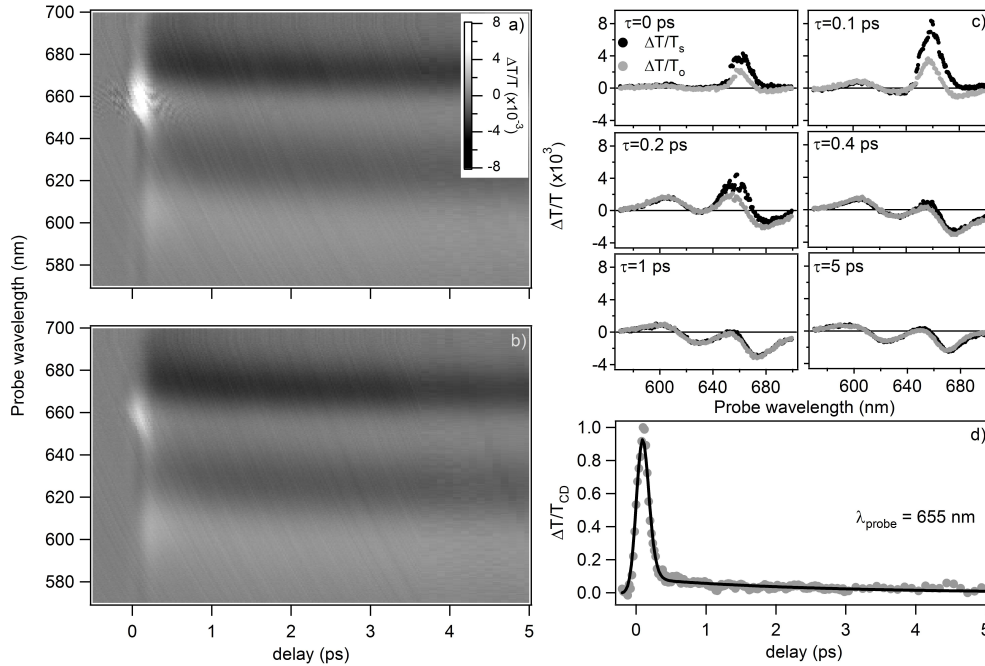


Figure 2. Transient variation of transmittivity maps measured at 77 K for various pump-probe delays and probe wavelengths. The probe pulse polarization has respectively the same (a) and opposite (b) helicity with respect to the pump beam. c) $\Delta T/T$ energy spectrum for co ($\Delta T_s/T$ black trace) and counter ($\Delta T_o/T$ gray trace) circularly polarized beams at different delays. d) The black dots are the difference between the $\Delta T_s/T$ and $\Delta T_o/T$ at the maximum value of the A exciton bleaching (i.e. around 655 nm), normalized to the unity. The continuous line is the fit of the data to a bi-exponential decay function convoluted with a gaussian accounting for the temporal resolution of the pump-probe experiment.

relaxation of the valley polarization after the resonant excitation of the A exciton has been simulated by solving the kinetic spin Bloch equations¹⁶, neglecting the short range part of the exchange interaction and it is in good agreement with the measured fast decay τ_1 . The small magnetic field associated to the long range part of the exchange interaction is believed to be responsible of the slower decay τ_2 of the valley polarization.

We further study the valley depolarization dynamics by TRCD measurements (see fig.2). In this experiment the valley unbalance is created by a circularly polarized pump pulse while the transient variation of the absorption is measured by a probe pulse characterized by the same and opposite helicity. The difference between the optical non-equilibrium response measured within these two configurations gives access to the intervalley scattering processes. Both the 2D map reported in fig.2a,b are characterized by the bleaching of the A and B optical transition. We observe a vanishing TRCD signal in the spectral window centered around the B exciton transition, while around the A exciton the optical response is characterized by a pronounced anisotropy lasting for few ps. The difference between the $\Delta T_s/T$ and $\Delta T_o/T$ at the maximum value of the A exciton bleaching, reported in fig.2d, decays exponentially with two time scales. The first time constant is below the temporal resolution of the pump-probe experiment while the slower one is on the order of few ps. This result is in complete agreement with the decay constants measured by TRFR experiments. For this reason TRFR and TRCD are promising tool to study the valley relaxation dynamics in 2D transition metal dichalcogenides.

4. CONCLUSION

In conclusion, we presented a complete study of the intervalley scattering dynamics of optically injected excitons in monolayer MoS₂ by combining two complementary techniques, TRCD and TRFR. We find that the characteristic time scales of the intervalley scattering processes are respectively $\tau_1 \sim 200$ fs and $\tau_2 \sim 5$ ps. The rapid valley depolarization dynamics is conform with an electron-hole exchange mechanism which couples the two different

valley configurations. These results set the standards for engineering of spintronic and valleytronic devices based on single layer TMDCs.

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