Effect of Substrate on Valley Relaxation Dynamics in Monolayer WS_2

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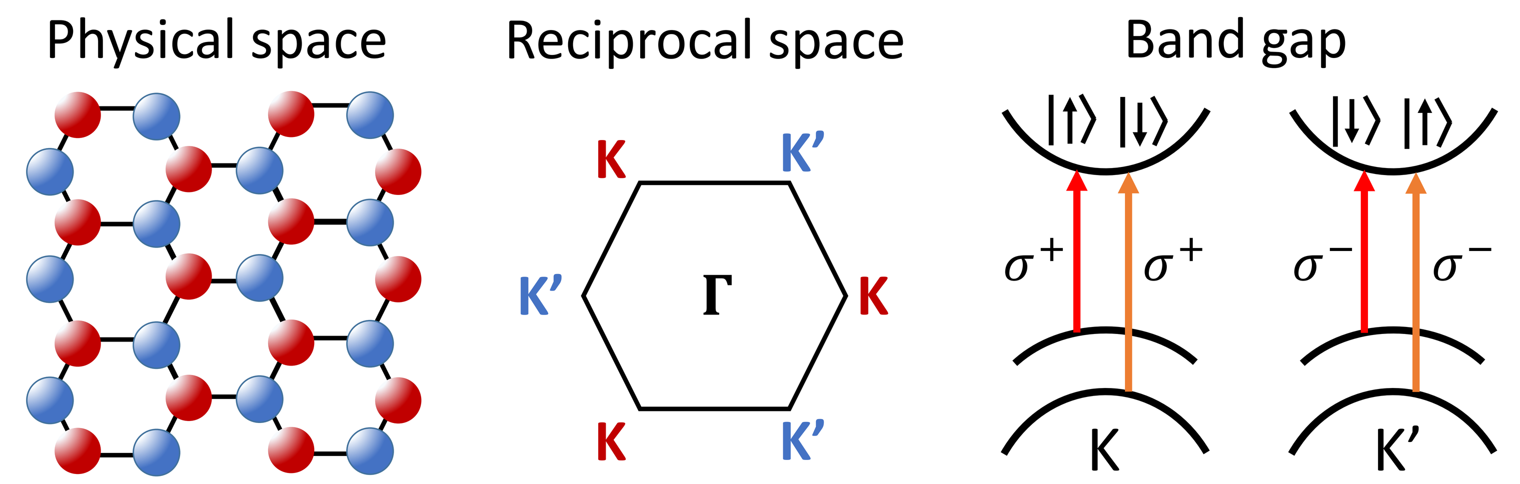
Abstract

Their large bandgaps and ability to be reduced to a single layer make transition metal dichalcogenides (TMD) ideal for future FET applications. In TMDs, electrons can be selectively excited into a particular valley in the conduction band due to lattice symmetry properties. Relaxation between valleys can then occur, and the time scale of this relaxation determines the viability of using these materials for valleytronic applications, which would attempt to use valley index to store/manipulate information. Any application of TMDs will undoubtedly consist of TMD layers supported by a substrate, however the effect of substrate on valley relaxation in these materials is hardly understood. Using ultrafast transient absorption spectroscopy, we measure valley lifetime on supported and suspended samples of monolayer WS_2. We find that valley lifetime is extended by an order of magnitude in suspended samples, thus demonstrating for the first time the large effects of substrate on valley relaxation.

Introduction

TMD Theory Basics:

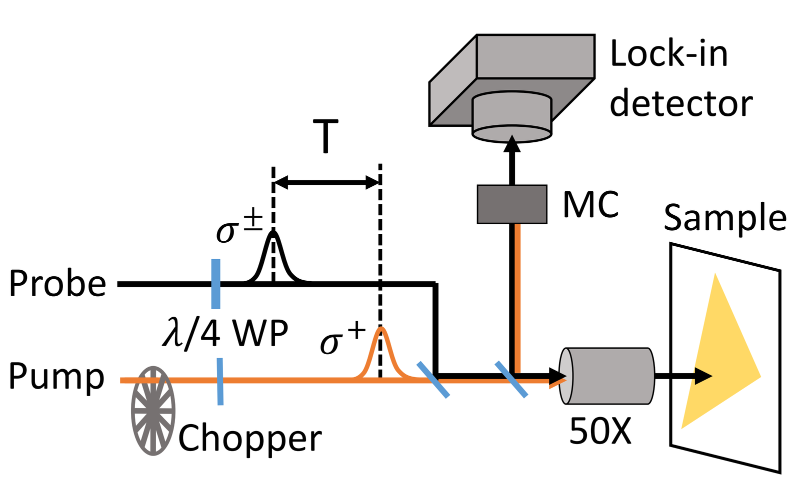


Hexagonal structure similar to graphene but with broken P symmetry.

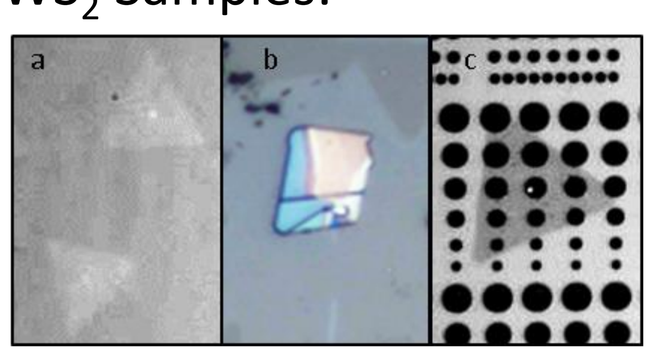
Bandgap occurs at K and K'=-K points in reciprocal space.

Excited spin, valley, energy, and layer [1] are coupled and can be selectively excited using C-polarized light.

Experiment Setup:

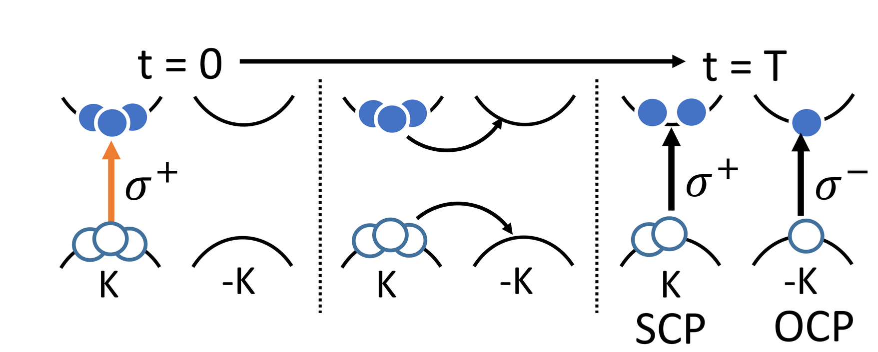


WS_2 Samples:



(left-to-right) As grown on Sapphire, transferred to hBN, and suspended over holes in SiO_2. **All samples held at 76K unless otherwise specified.**

Measurement:



Valley relaxation measurement: Pump pulse excites at t=0 and probe light of same (SCP) or opposite (OCP) C-polarization is transmitted at t=T.

We measure reflection with pump off, R, and pump on, R', and calculate differential reflection:

$$\frac{\Delta R}{R} = \frac{R' - R}{R}$$

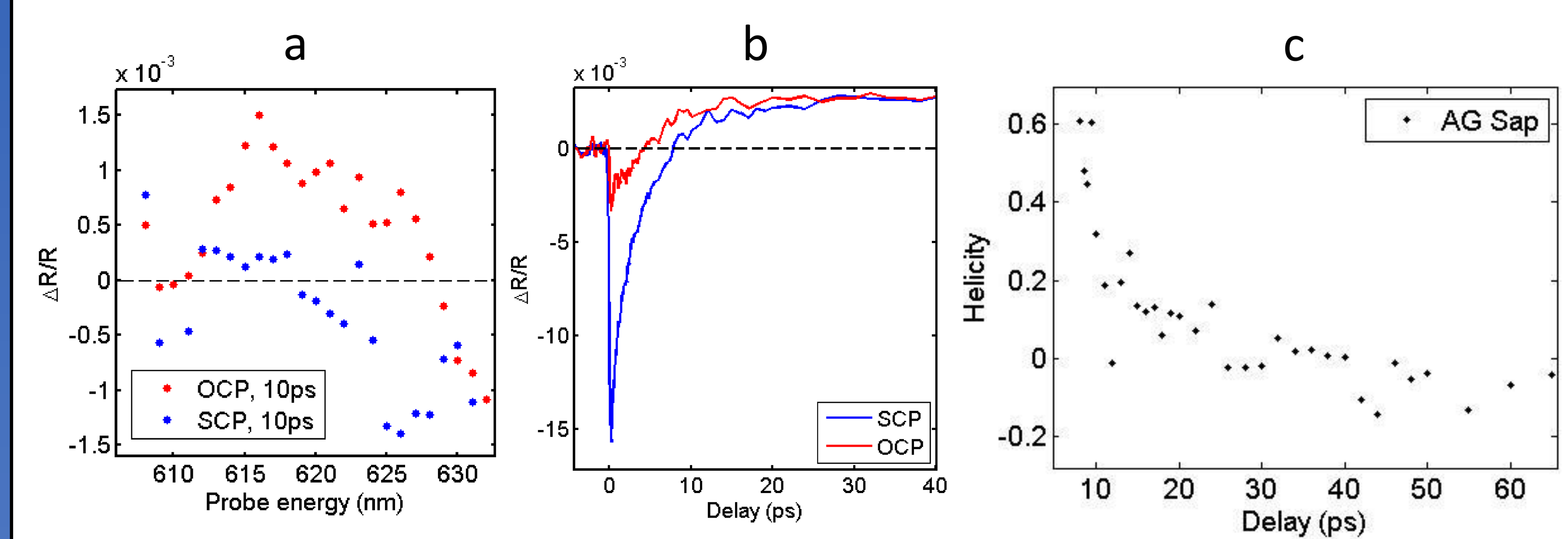
Valley Relaxation Results

Procedure:

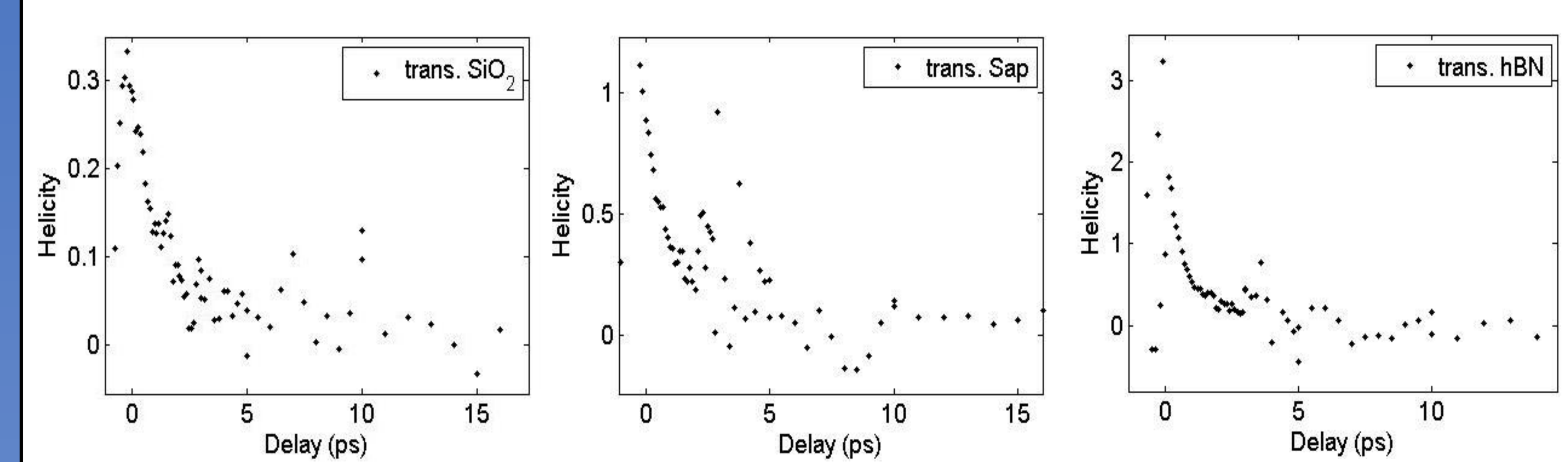
(a) Take SCP and OCP spectrum at late delay (to avoid spectral shifts of early delay) and (b) use a probe wavelength at which SCP-OCP difference is large to scan delay between pump and probe to produce dynamics data. (c) Calculate and fit helicity decay dynamics.

Use helicity as a measure of valley polarization [2]:

$$\rho \equiv \frac{SCP - OCP}{SCP + OCP}$$



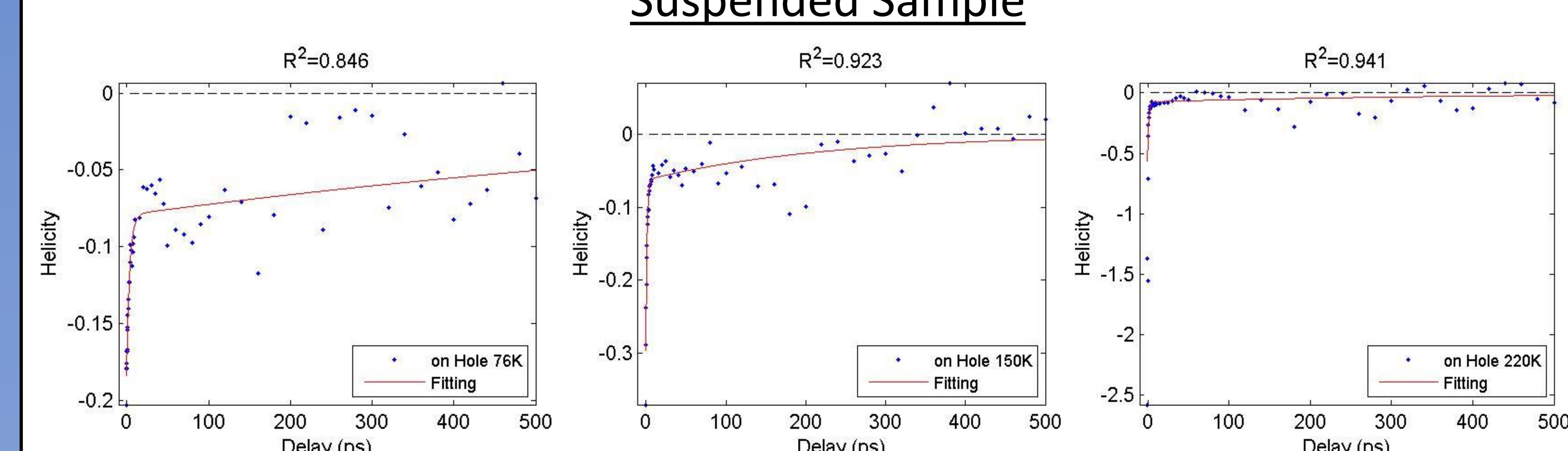
Transferred Supported Samples



Sample	A (a.u.)	τ (ps)
As-grown Sap	2.27	5.61
Trans. hBN	1.86	0.96
Trans. Sap	0.88	1.31
Trans. SiO2	0.28	1.74

- Single-exponential decays.
- AG Sap shows highest and longest helicity.
- Trans. SiO2 shows longest helicity of trans. samples.
- Trans. hBN shows highest (but shortest) helicity of trans. samples.

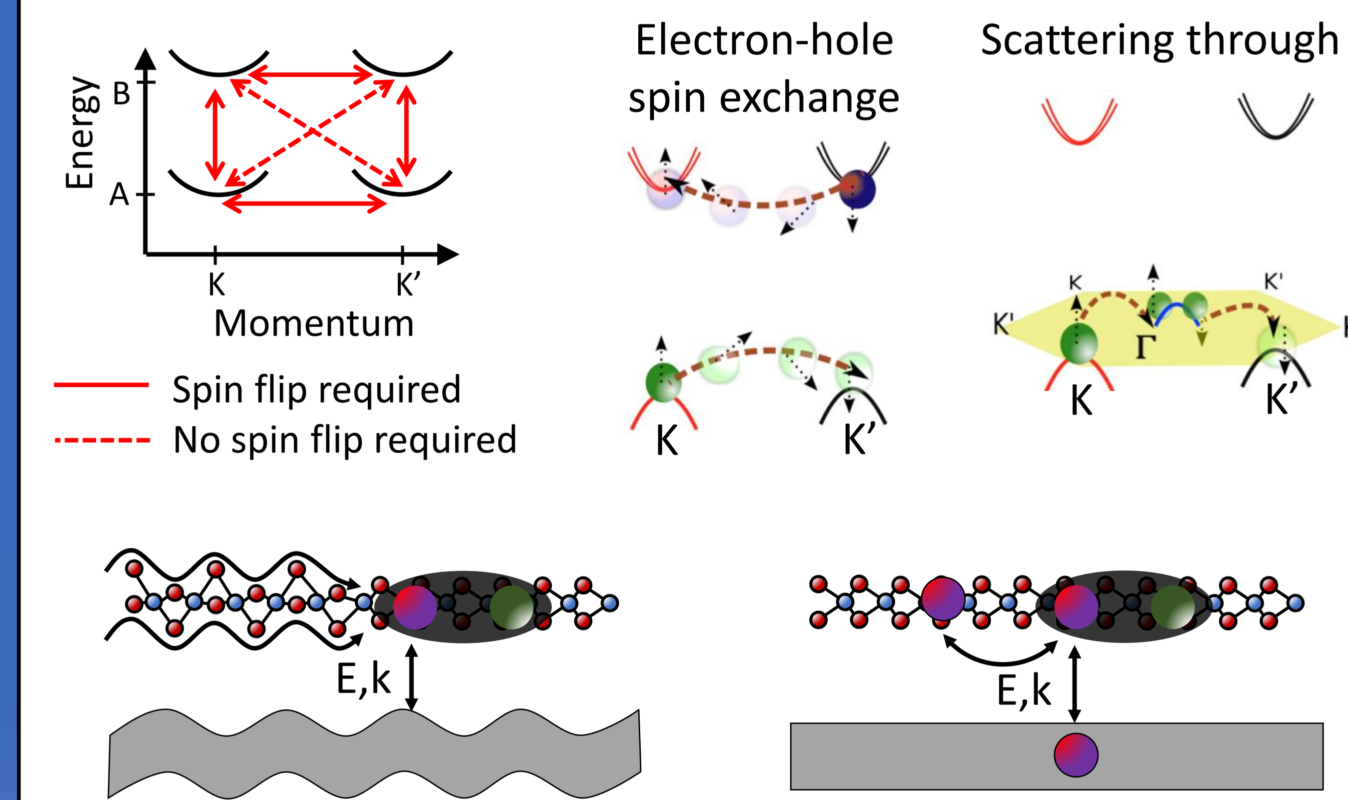
Suspended Sample



Temp. (K)	A_1 (%)	τ_1 (ps)	A_2 (%)	τ_2 (ps)	$A_1 + A_2$ (a.u.)
76	54	3.80	46	1097	0.17
150	75	1.41	25	228	0.25
220	84	1.38	16	368	0.47

- Long-lasting (>500ps) helicity at 76K!
- Double-exponential decays.
- Weight of short component increases with temperature.
- Strangely, A1+A2 (max helicity) is largest for the highest-temperature sample.

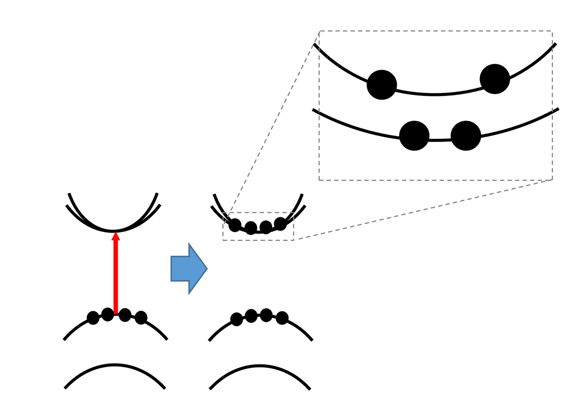
Valley Relaxation Mechanisms



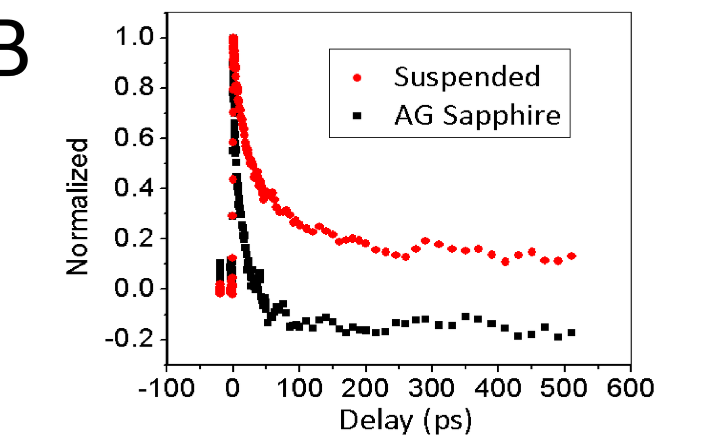
E, k exchange between carriers and **phonons** in monolayer and substrate.

E, k exchange between carriers and **defects** in monolayer and substrate.

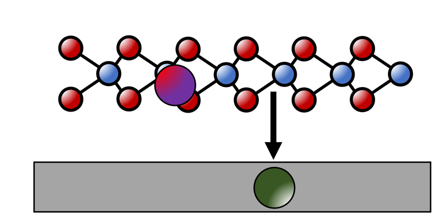
Pump A, Probe B



Valleys are split due to SOC. Electrons can flip spin but holes cannot due to energy barrier.



Fast decay component in supported MoS_2 represents hole-only relaxation.



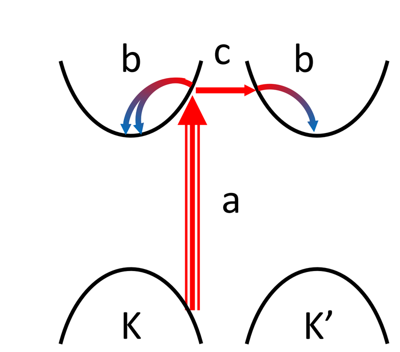
Possible hole transfer into substrate.

Conclusion

We find that valley lifetime in suspended monolayer WS_2 exceeds 500ps at 76K and thus conclude that substrate greatly increases valley relaxation rate. Our findings suggest that whether or not TMDs can be applied in spintronic/valleytronic devices depends largely on future efforts to optimize substrate.

Future Research

- Modeling of temp. dependence.
- Analysis of spectral differences.
- Transient absorption and valley relaxation at edge states..
- Pump-fluence dependence of valley relaxation in suspended sample.
- Pump-energy dependence of valley relaxation in suspended sample (see figure to the right).



a) Excitation of hot excitons
b) Cooling
c) Valley scattering

References

[1] X. Xu, W. Yao, D. Xiao, and T. F. Heinz, Nat. Phys. **10**, 343 (2014)
[2] K. F. Mak, K. He, J. Shan, T. F. Heinz, Nat. Nano. **7**, 494 (2012)