Monolayer semiconductors:
Valley dynamics & ‘valley noise’

(Or, what can we learn about dynamics… without ever actually perturbing the system?)

Yesterday: Excitons/optoelectronics
Not much valley stuff
Static measurements, high B

Today: Valley *dynamics (ps -> μs)*
Ultrafast optics, not much B
Noise (& quantum measurement)

Scott Crooker
NHMFL Los Alamos

Quantum Science Summer School, Penn State University

Useful / interesting review-type papers on monolayer TMDs (with an emphasis on optics and/or valleytronics):

Valleytronics in 2D materials
JR Schaibley, H. Yu, G. Clark, P. Rivera, J. S. Ross, K. Seyler, W. Yao, X. Xu
Nature Reviews Materials **1**, 16055 (2016)

Light-valley interactions in 2D semiconductors
KF Mak, D. Xiao, J. Shan
Nature Photonics **12**, 451 (2018)

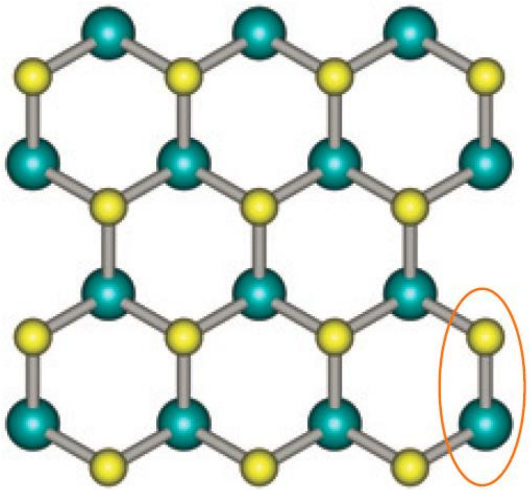
Why all the fuss about 2D semiconductors?
Andres Castellanos-Gomez
Nature Photonics **10**, 202 (2016)

Photonics and optoelectronics of 2D semiconductor TMDs
K. F. Mak and J. Shan
Nature Photonics **10**, 216 (2016)

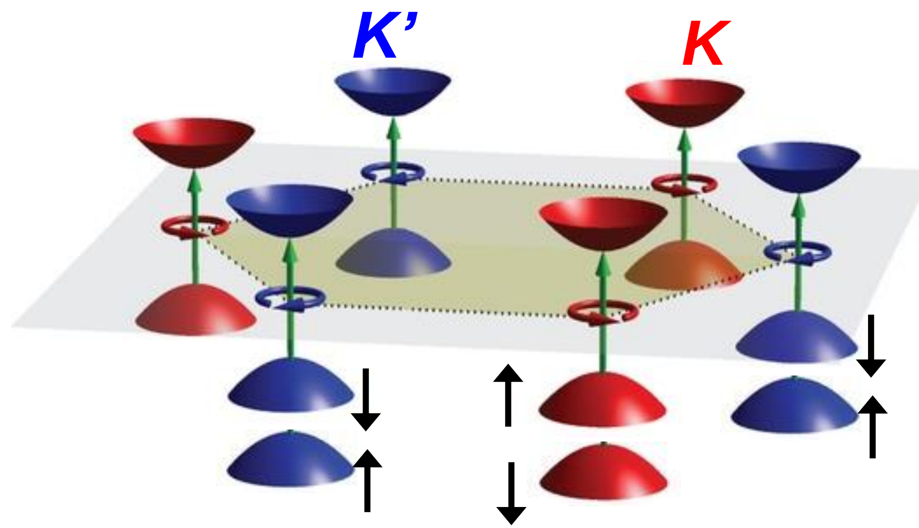
Spins and pseudo-spins in layered TMDs
Xiaodong Xu, Wang Yao, Di Xiao, Tony F. Heinz
Nature Physics **10**, 343 (2014)

Van der Waals heterostructures
A. K. Geim and I. V. Grigorieva
Nature **499**, 419 (2013)

Reminder: 'Valley pseudospin' & valleytronics



-from X. Xu *et al., Nat. Phys*. **10**, 343 (2014)



Key point: lack of inversion + SOC: *spin-valley locking*

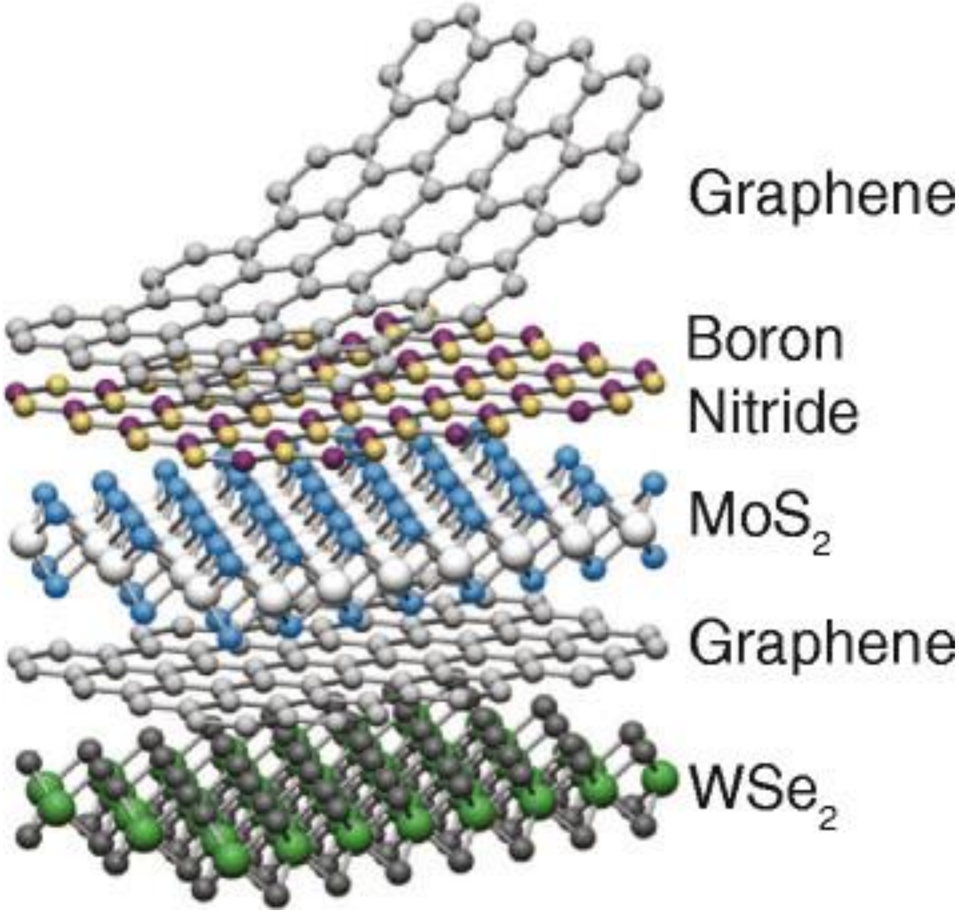
RCP & LCP light couple *selectively* to *K* & *K'* valleys

Easy optical access to valley degrees of freedom

First paper: Di Xiao *et al., PRL* **108**, 196802 (2012)

Excellent reviews: J. Schaibley, X. Xu *et al*, *Nature Reviews* **1**, 16055 (2016)
X. Xu, D. Xiao, W. Yao, & T. Heinz, *Nat. Physics* **10**, 343 (2014)
K. F. Mak, D. Xiao, & J. Shan, *Nat. Photonics* **12**, 451 (2018)

“Valleytronic” devices based on 2D TMDs?



We still need to know:

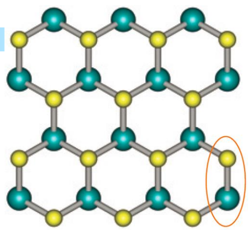
1) Spin & valley relaxation?

2) Resident carriers (*not* excitons)

3) Electrons vs. holes?

Geim & Grigorieva, Nature **499**, 419 (2013)

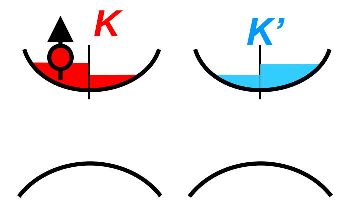
Today: Spin/valley dynamics in monolayer TMD semiconductors



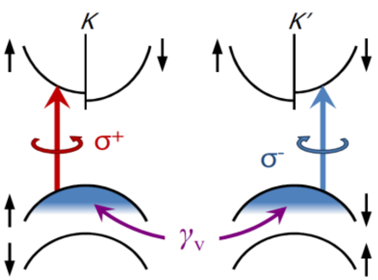
Outline:

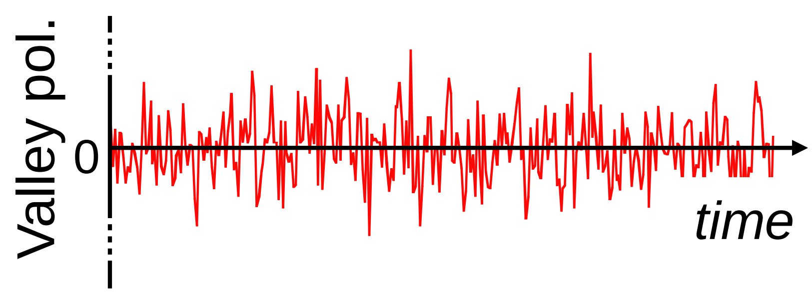
- **Brief history of "robust valley degree of freedom" in ML TMDs**
  - *photoluminescence of (short-lived) excitons*

- **Spin/valley dynamics of *resident* electrons & holes**
  - *actually useful parameters for real quantum devices*
  - *μs valley polarization of holes (promising!)*

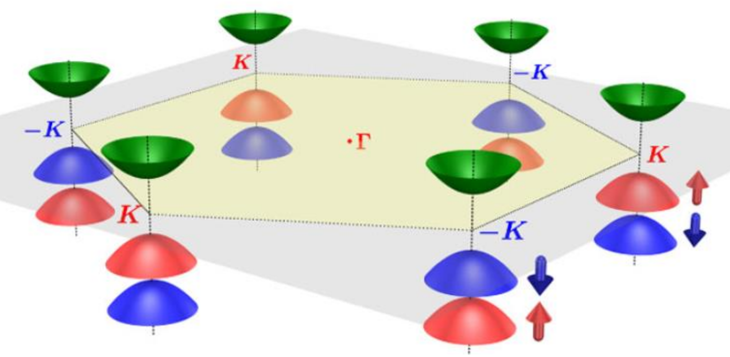


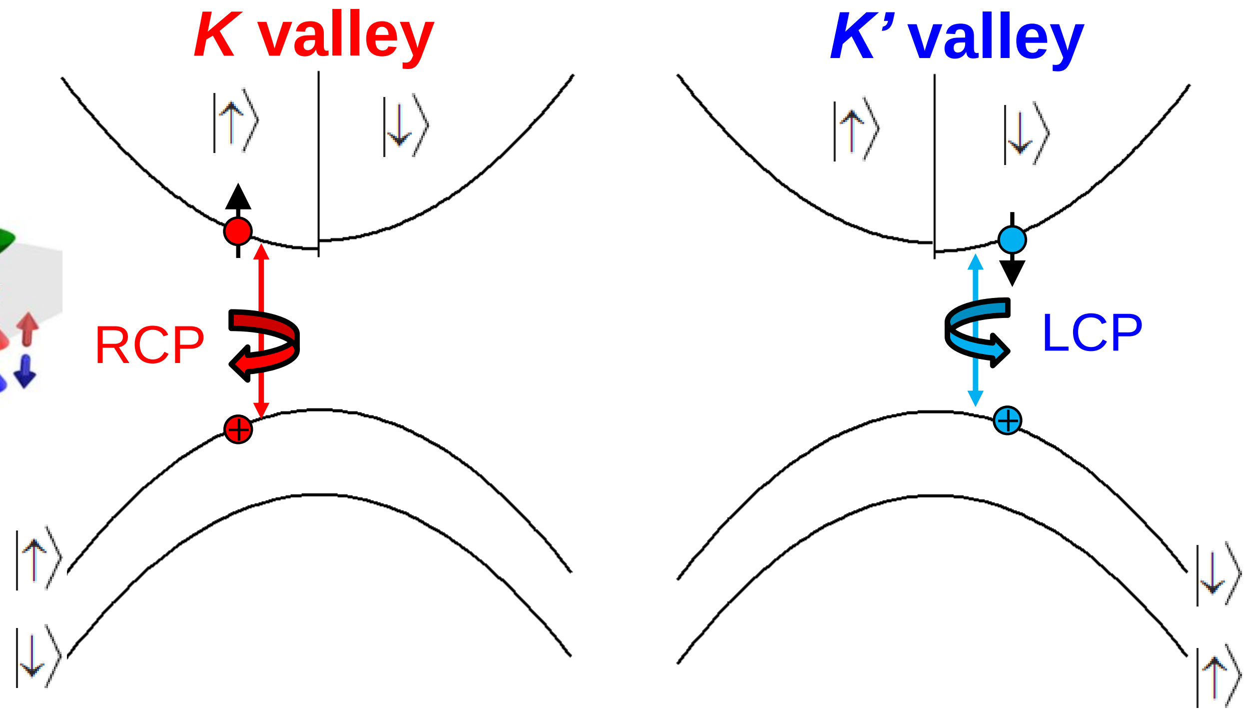
- **Spontaneous thermodynamic "valley noise" of electrons & holes**
  - *nonperturbative (quantum?) measurements based on fluctuations*
  - *"valley noise" reveals intrinsic valley dynamics*





Valley-polarized *excitons* in 2D semiconductors





- **Optical selection rules at *"A"* exciton:**
  RCP light couples to spin-up excitons in *K* valley
  LCP light couples to spin-down excitons in *K'* valley

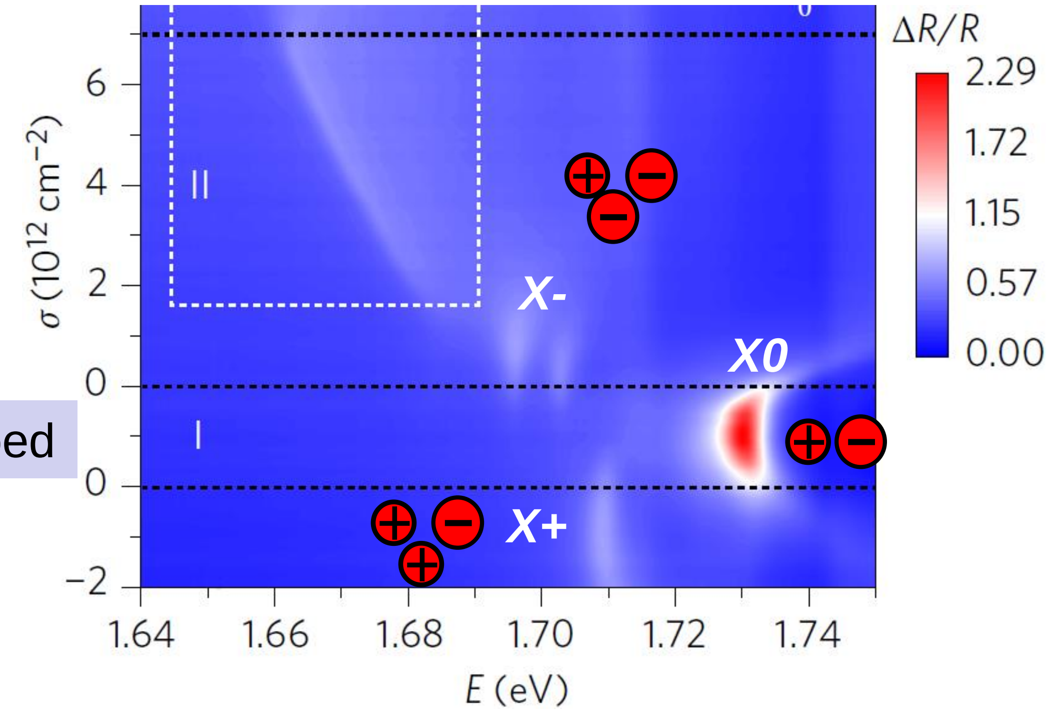
First paper: Di Xiao *et al.*, *PRL* **108**, 196802 (2012)
Excellent reviews: X. Xu, D. Xiao, W. Yao, & T. Heinz, *Nat. Physics* **10**, 343 (2014)
K. F. Mak, D. Xiao, & J. Shan, *Nat. Photonics* **12**, 451 (2018)

Also: Positively/negatively charged excitons

Electron-doped

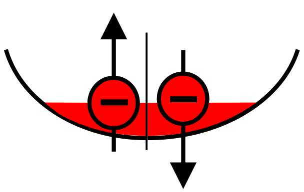
undoped

Hole-doped

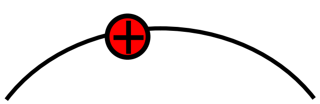


Absorption!
Real D.O.S.!

From Wang, Shan, & Mak, *Nature Nanotech.* **12**, 144 (2017)



Trion absorption depends *explicitly* on the density of resident carriers. *No resident carriers -> no trion D.O.S.*

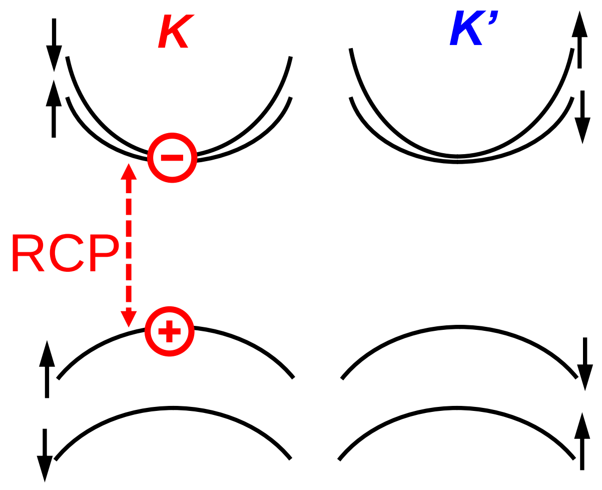


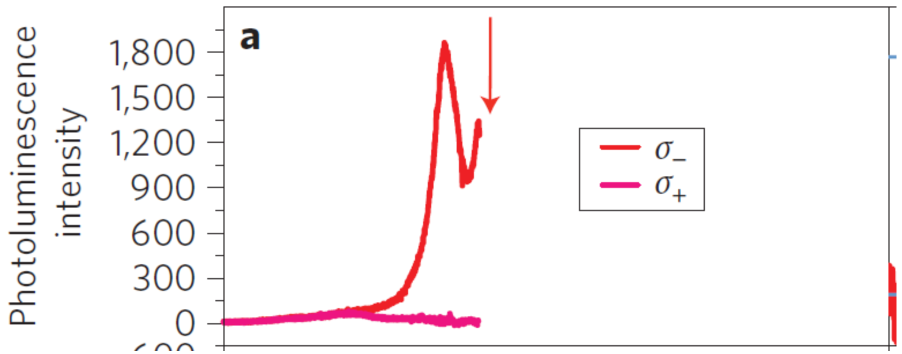
Key point:

Signals at *trion* energy should tell us about polarization of Fermi sea.

Initial PL studies suggested robust valley pol.

In 2012, several groups studied circularly-polarized photoluminescence of monolayer MoS_2. PL was <u>co-polarized</u>.





Cao et al., *Nature Commun*. **3**, 887 (2012)
Zeng et al, *Nature Nanotech*. **7**, 490 (2012)
Mak et al, *Nature Nanotech*. **7**, 494 (2012)
Sallen et al., *PRB* **86**, 081301 (2012)

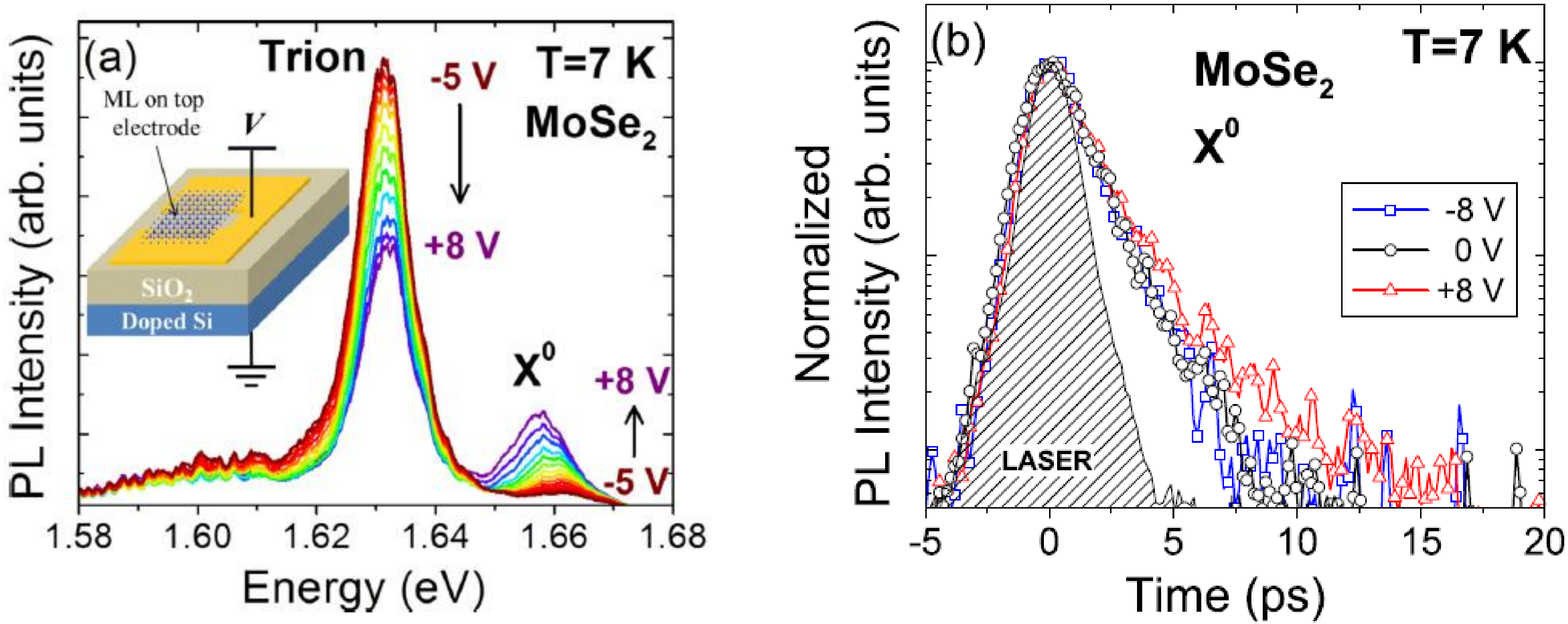
But : photoluminescence is a (nonequilibrium) exciton effect
So -- either exciton valley relaxation is indeed slow ("robust")

…or…

maybe excitons are just really short-lived

Indeed: Exciton recombination is really fast!

e-h recombination lifetimes <10 ps at low temperatures

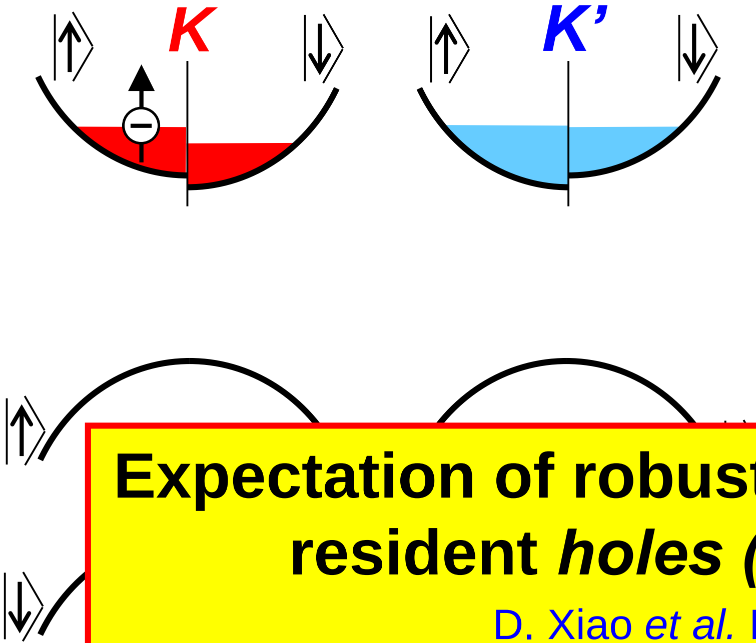


[data from C. Robert, B. Urbaszek, X. Marie *et al.*, PRB **93**, 205423 (2016)]

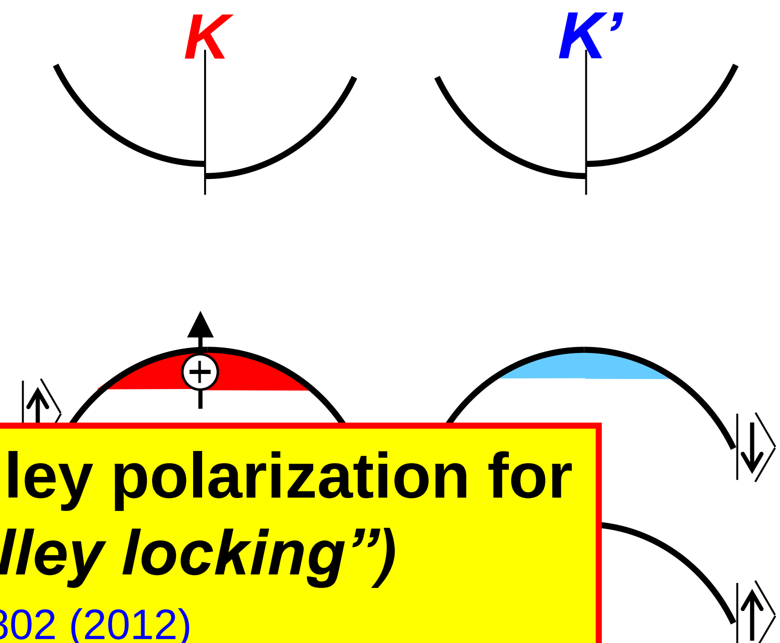
There are many interesting ultrafast studies of the fs & ps dynamics of excitons (*K* -> *K'* scattering, coherence effects, etc…

A very different (& very important!) question:
Spin/valley dynamics of *resident electrons* & *holes?*

Electron-doped (*n*-type) regime



Hole-doped (*p*-type) regime



Expectation of robust spin/valley polarization for resident *holes (“spin-valley locking”)*

D. Xiao *et al.* PRL **108**, 196802 (2012)

Three pathways for electrons…

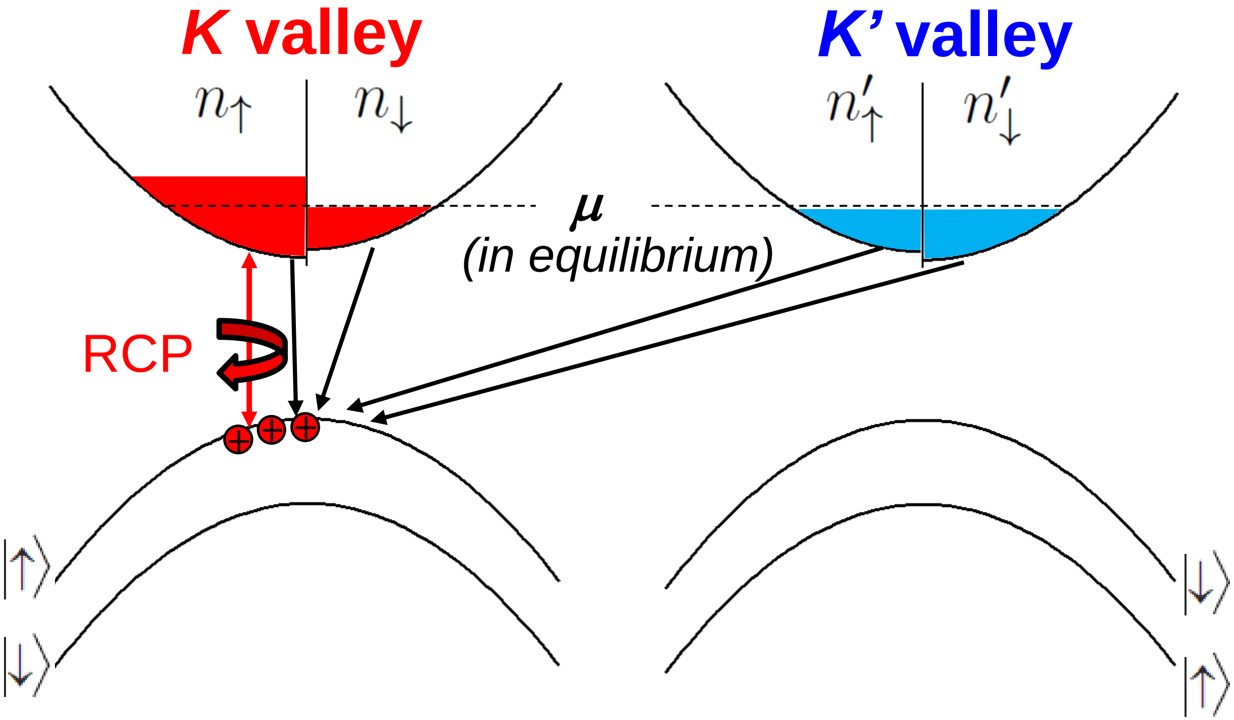
1) spin scattering within a valley
2) spin-*conserving* intervalley
3) spin-*flip* intervalley (slow)

ONE pathway for holes…

1) spin-*flip* intervalley (slow)

How to measure dynamics of *resident* carriers?

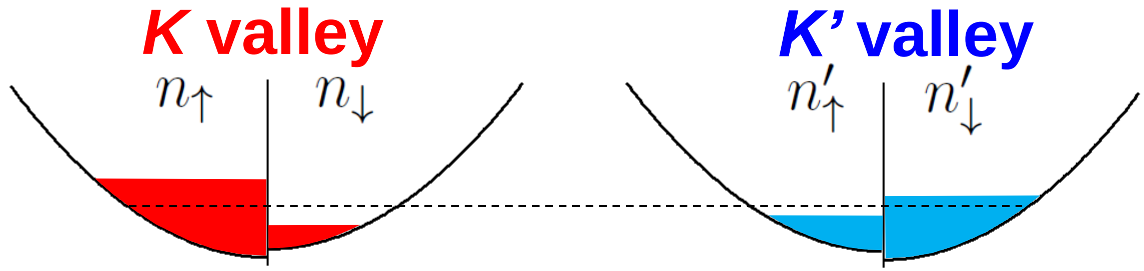
Conventional pump-probe (ultrafast optical) method:



- ***t<0***: resident carriers in equilibrium ($\mu_\uparrow = \mu_\downarrow = \mu'_\uparrow = \mu'_\downarrow$)
- ***t=0***: pump RCP at 'A' exciton
- ***t~0-100 ps:*** minority carriers recombine with resident carriers *(i.e., excitons & trions form & recombine)*

How to measure dynamics of *resident* carriers?

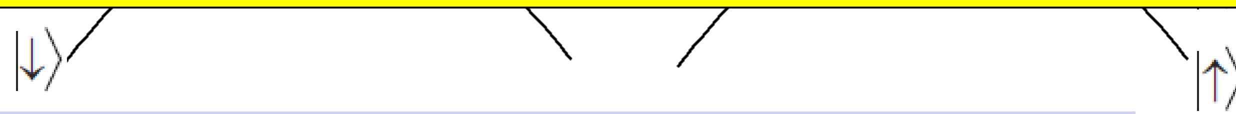
Conventional pump-probe (ultrafast optical) method:



Physics goal:

Measure spin & valley relaxation of these resident e- (or h+).

Time scales may be very long!



Key point:

t>100 ps*: Non*-equilibrium resident carriers *only*

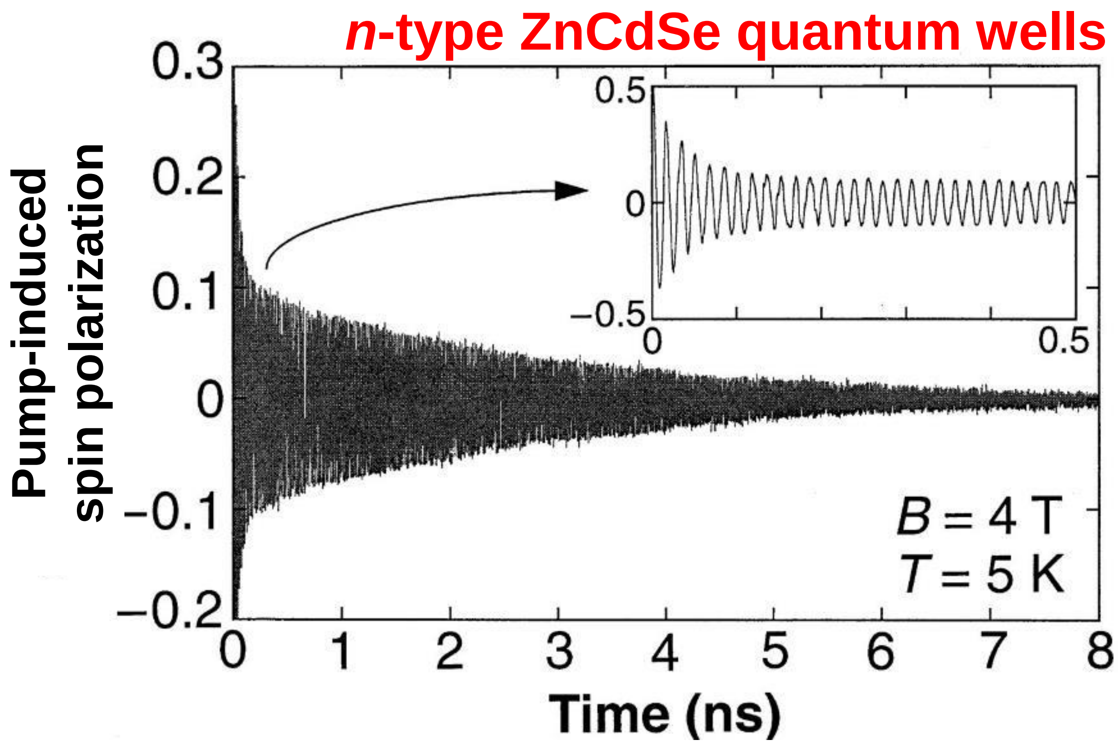
$\mu_\uparrow \neq \mu_\downarrow \neq \mu'_\uparrow \neq \mu'_\downarrow$

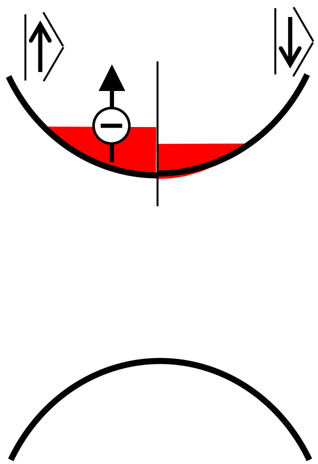
Spin polarization: $S_z = n_\uparrow + n'_\uparrow - n_\downarrow - n'_\downarrow$

Valley polarization: $N_v = n_\uparrow + n_\downarrow - n'_\uparrow - n'_\downarrow$

Historical interlude: early days of "spintronics"

"Room temperature spin memory in 2D electron gases"
Kikkawa, Samarth, Smorchkova, Awschalom, *Science* **277**, 1284 (1997)

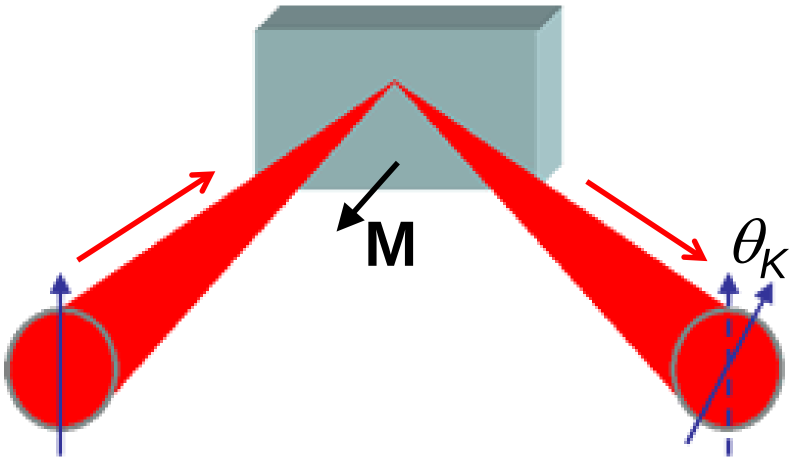


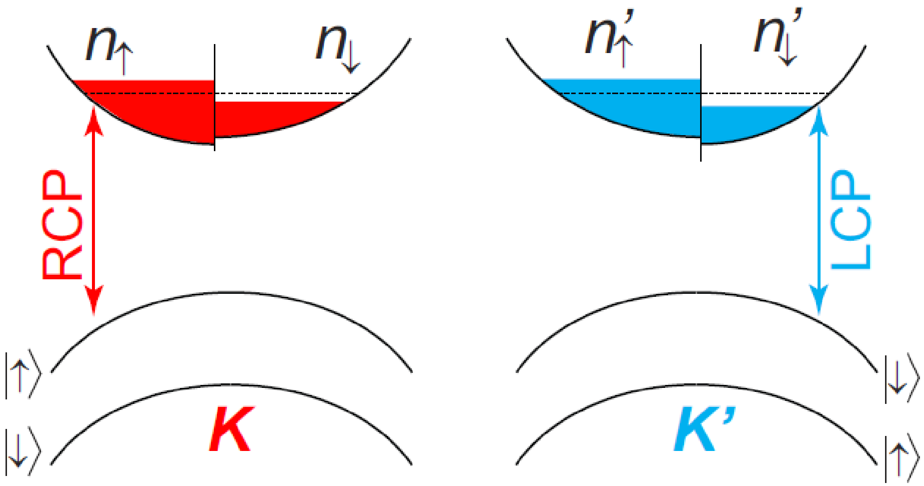


Exciton lifetime: <50 ps
Spin lifetime of resident electrons: 5 ns ! (At room temp!)

Detection: optical Kerr/Faraday rotation

A direct probe of the resident carrier polarization





Optical Kerr rotation, θ_K $\propto(\alpha_{RCP}-\alpha_{LCP})$

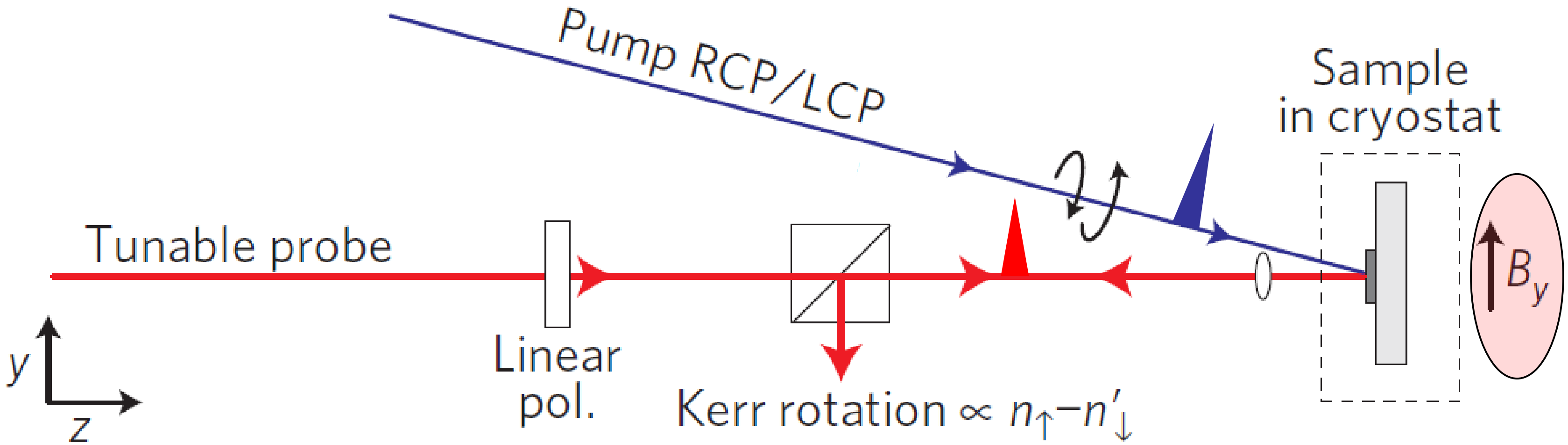
$\updownarrow$ = |RCP> + |LCP>

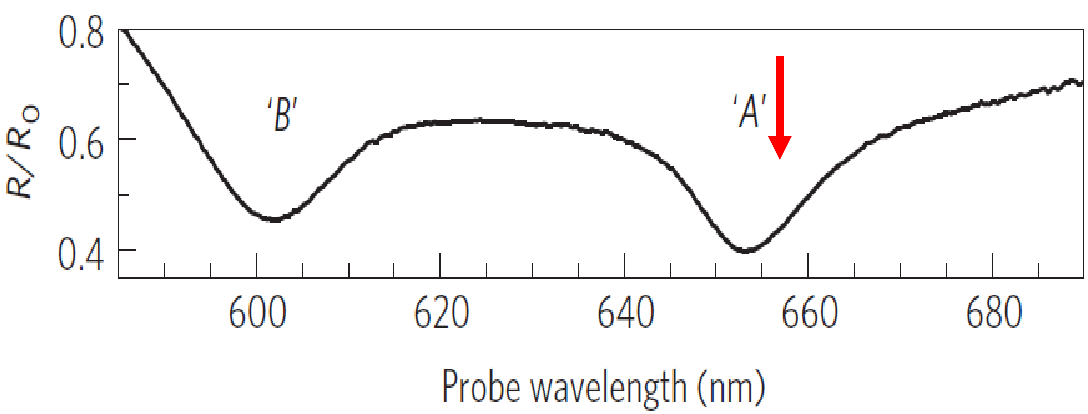
$\theta_K \sim (n_\uparrow - n'_\downarrow) \sim (S_z + N_v)/2$

Measure carrier spin/valley polarization...

…long after minority species are gone

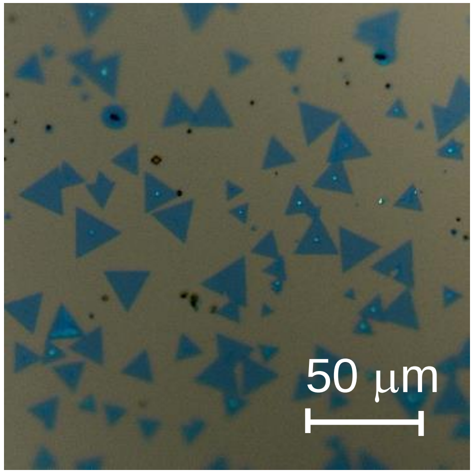
Experiment: Time-resolved Kerr rotation of MoS_2



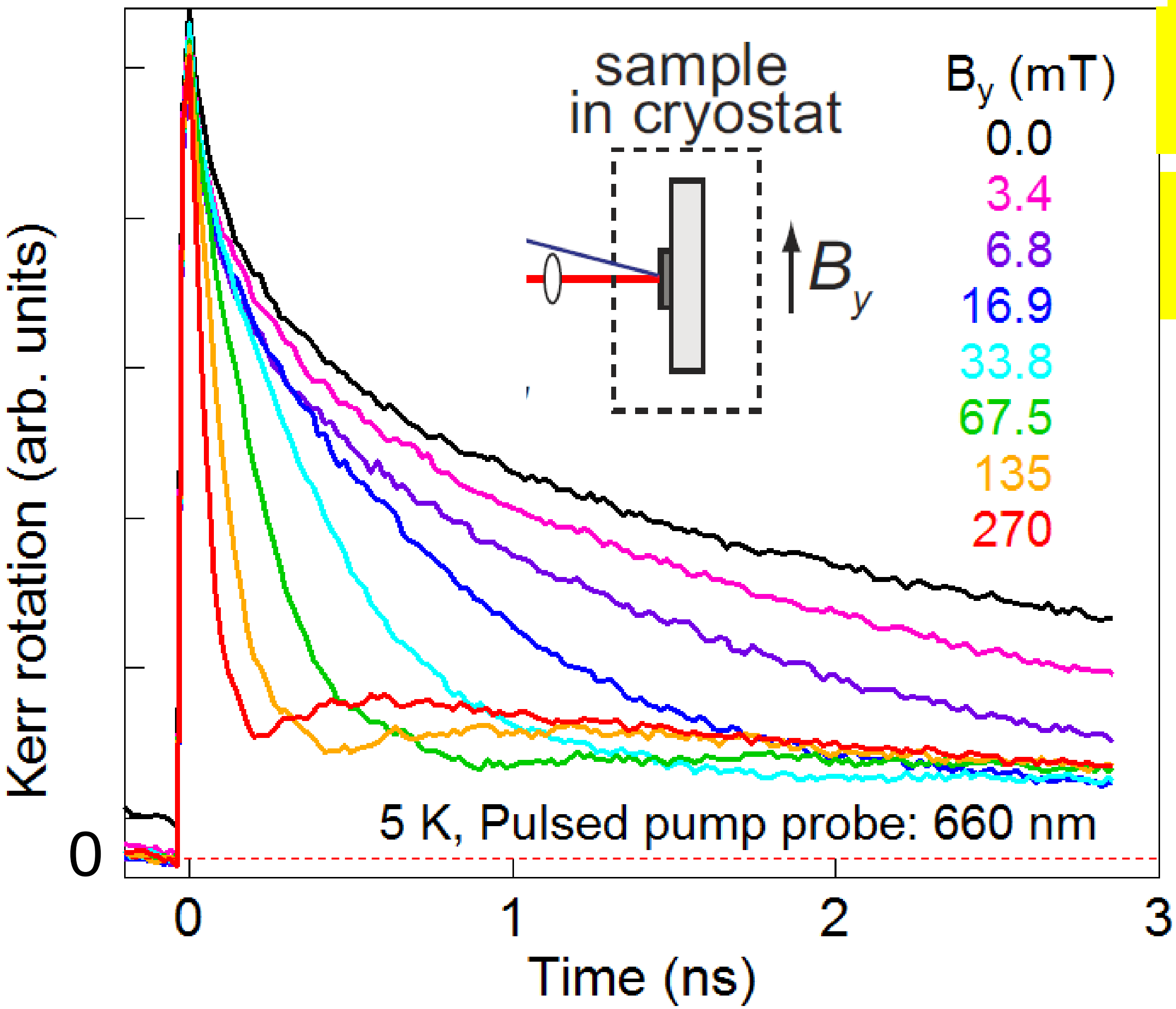


/ CVD

^{2} cm^{-2}

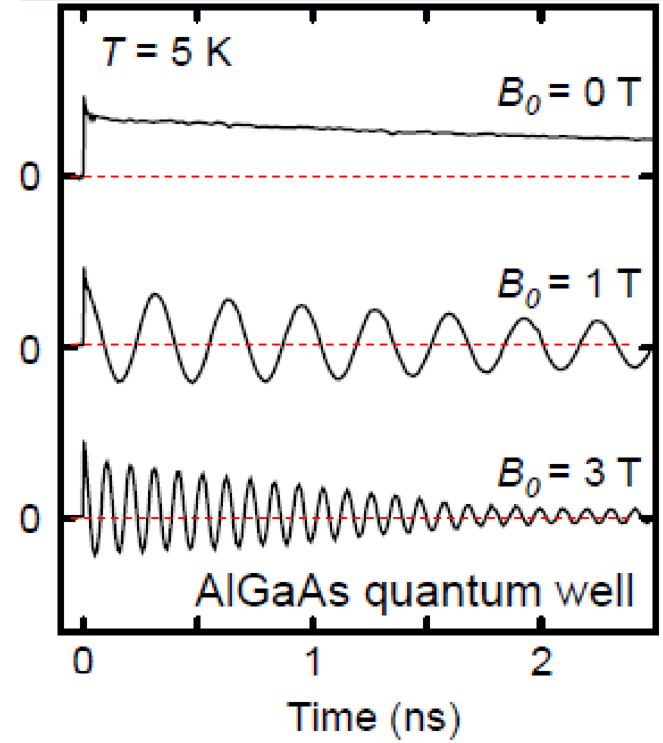


Time-resolved Kerr rotation of MoS_2



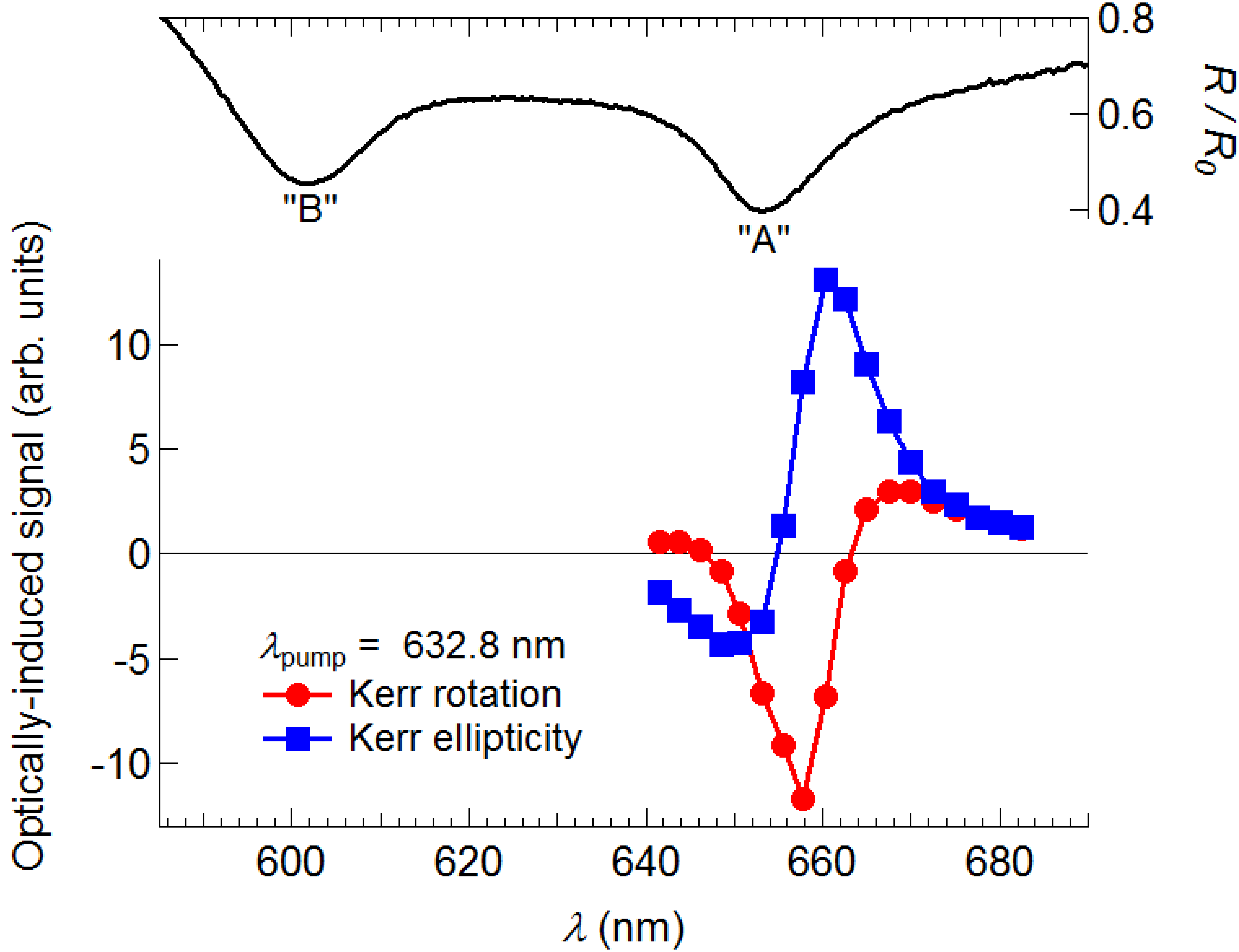
- ~3 ns decay at B_y=0
- small B_y: faster decay (spin relaxation)
- **BUT**: no prominent spin precession.

Different than, *e.g.*, GaAs

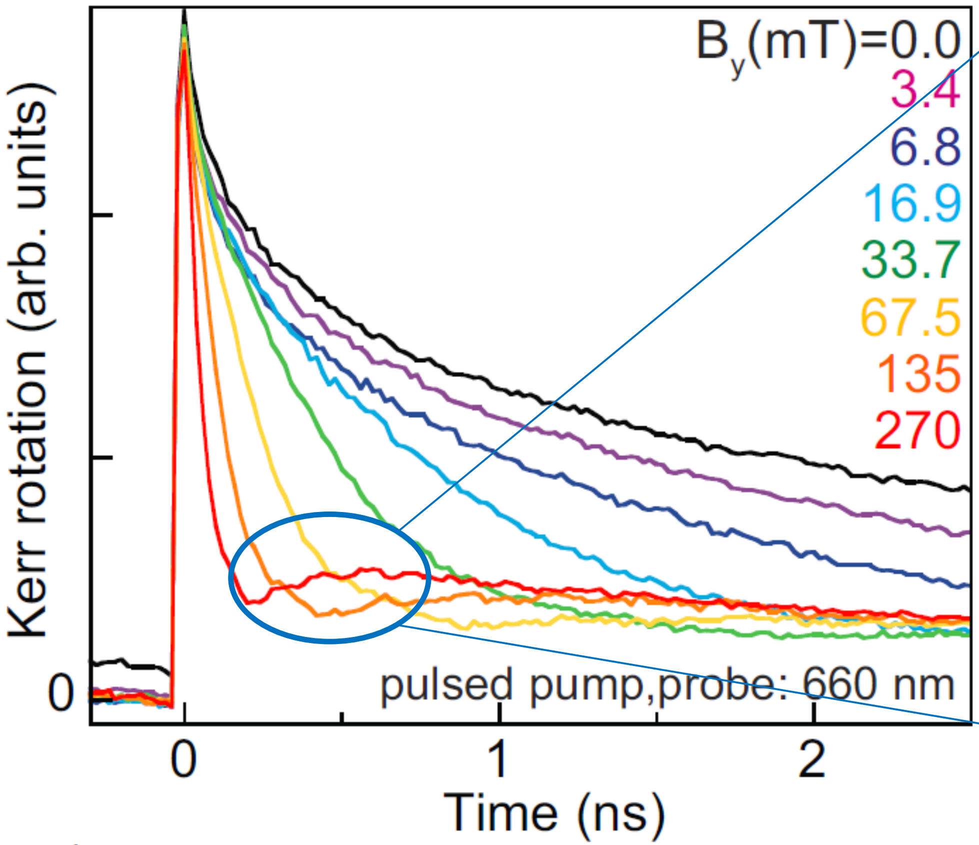


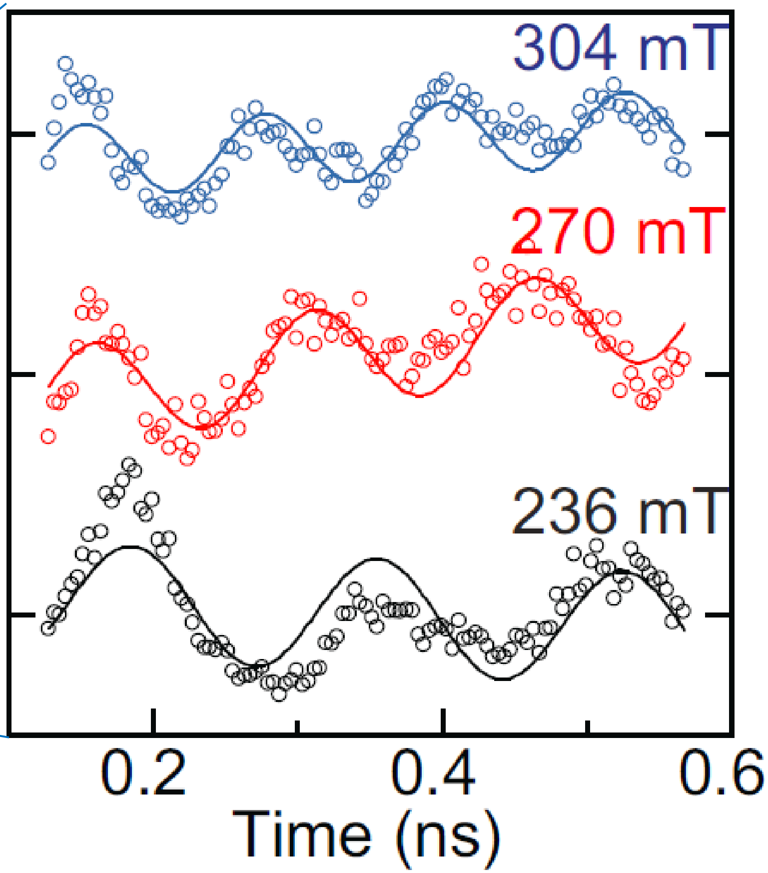
Yang et al, Nature Physics **11**, 830 (2015)

Spectral dependence of Kerr signals



Actually… some (tiny) coherent spin precession

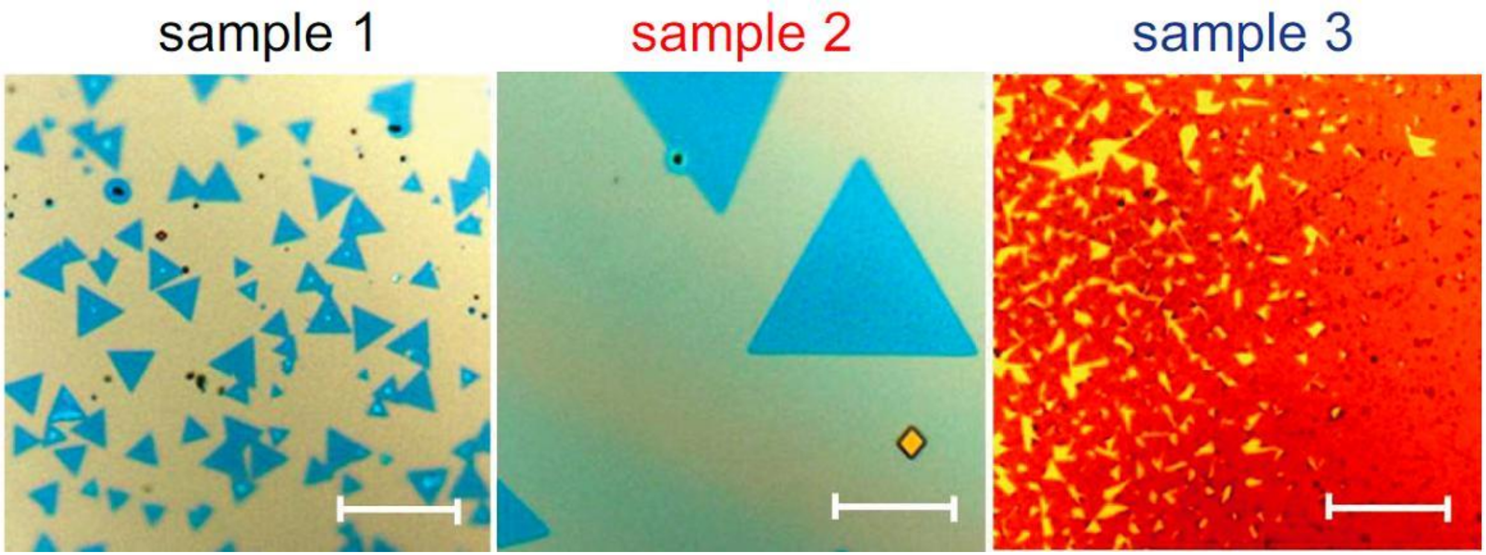




***Some* electrons undergo coherent spin precession.**

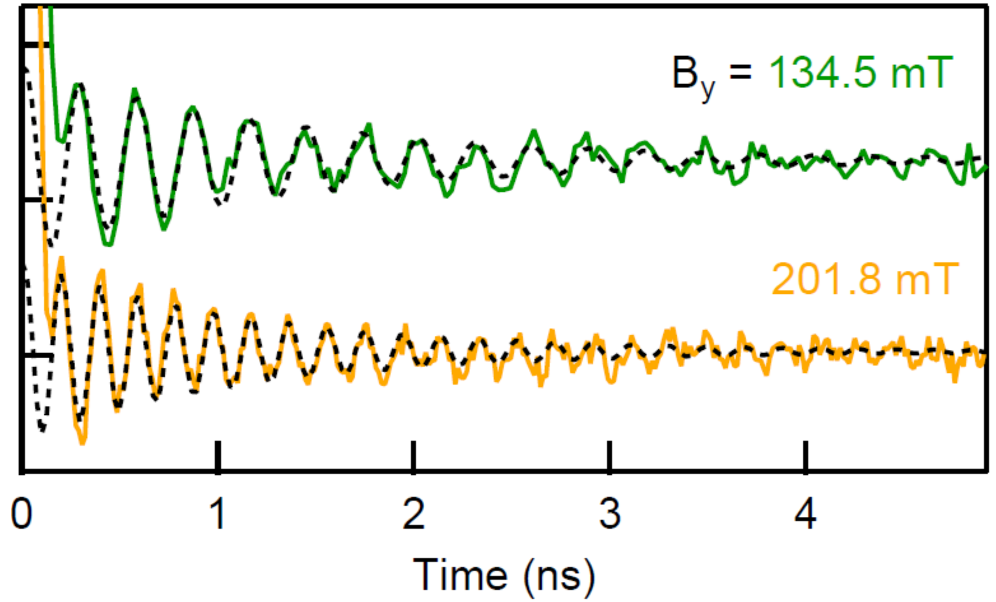
Localized electrons?

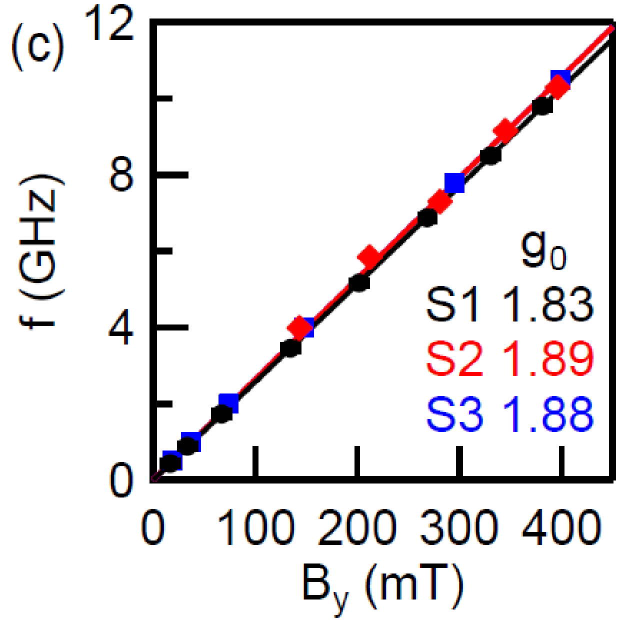
Different MoS2 samples grown by CVD



Rice U. Rice U. NRL

Coherent spin precession of (localized?) electrons





Spin coherence persists for nanosec.

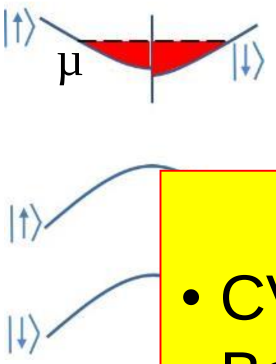
Precession frequency increases *linearly* with applied field: **g~1.85**

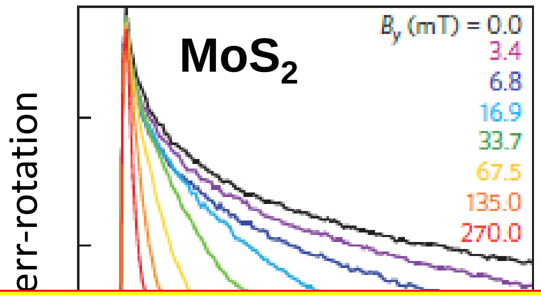
Sub-ensemble of localized electrons?

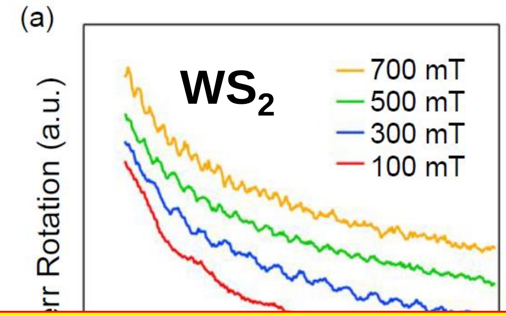
Nano Letters **15**, 8250 (2015)

Initial studies of resident carrier dynamics

***n*-type**







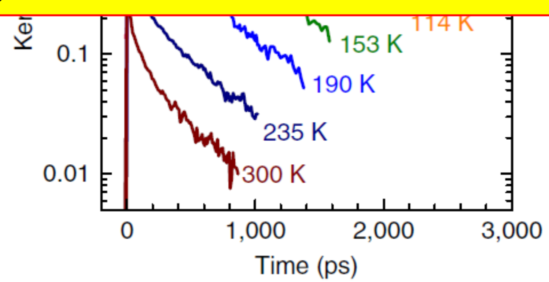
18)

***p*-ty**

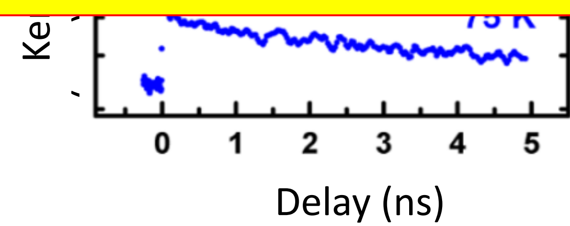
However…

- CVD-grown monolayers *(not exfoliated crystals)*
- Background carrier densities were fixed & not tunable
- Due to uncontrolled impurities
- Systematic trends difficult to identify

Need: Dynamic studies in a single *charge-tunable* gated device

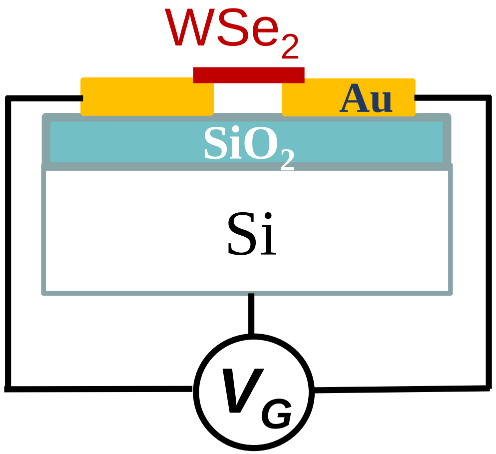


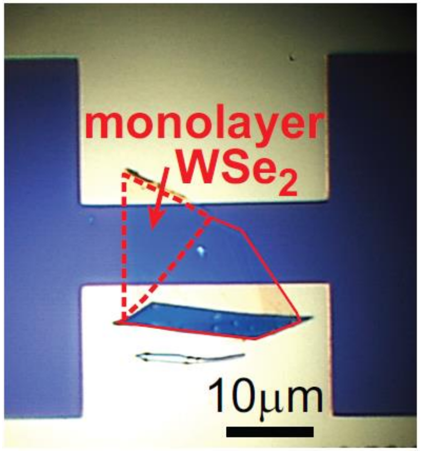
Hsu, *Nat. Comm.* **6**:8963 (2015)



Song, *Nano Lett.* **16**, 5010 (2016)

Gated single monolayers of exfoliated WSe_2

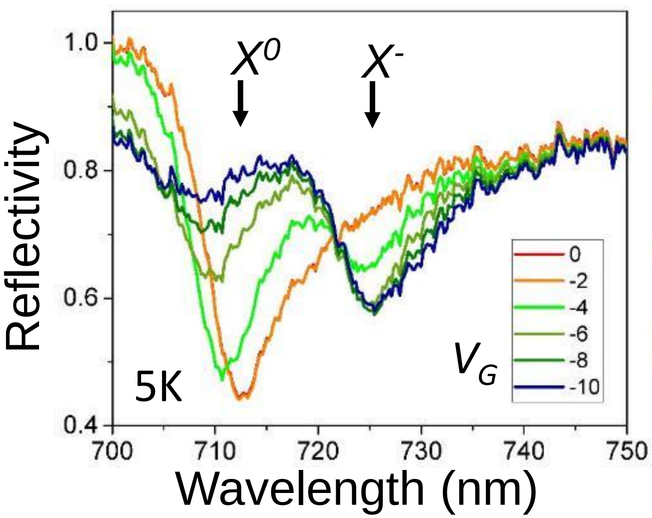


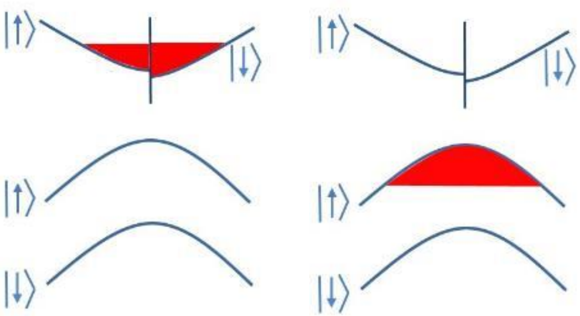


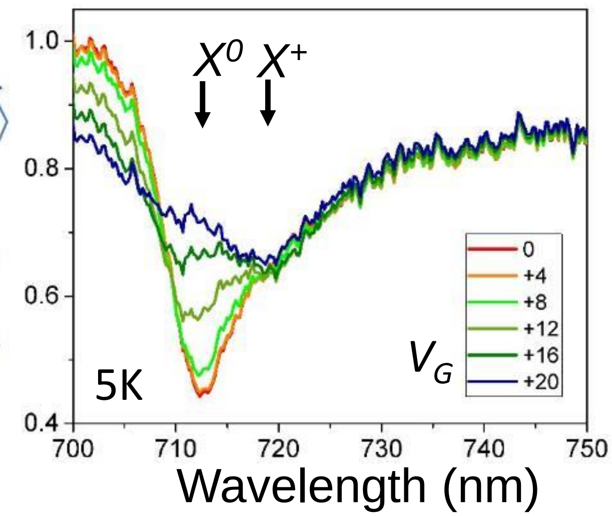
Cedric Robert
(INSA-Toulouse)

Electron-doped regime

Hole-doped regime



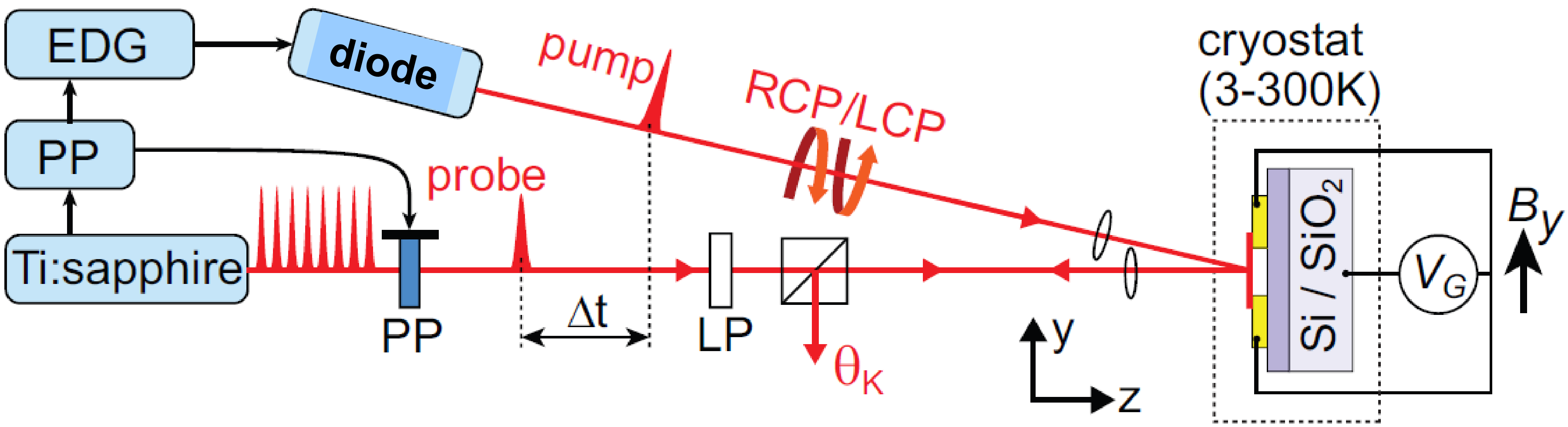




P. Dey *et al.*, PRL **119**, 137401 (2017)

Experiment: Time-resolved Kerr rotation

P. Dey *et al.*, PRL **119**, 137401 (2017)



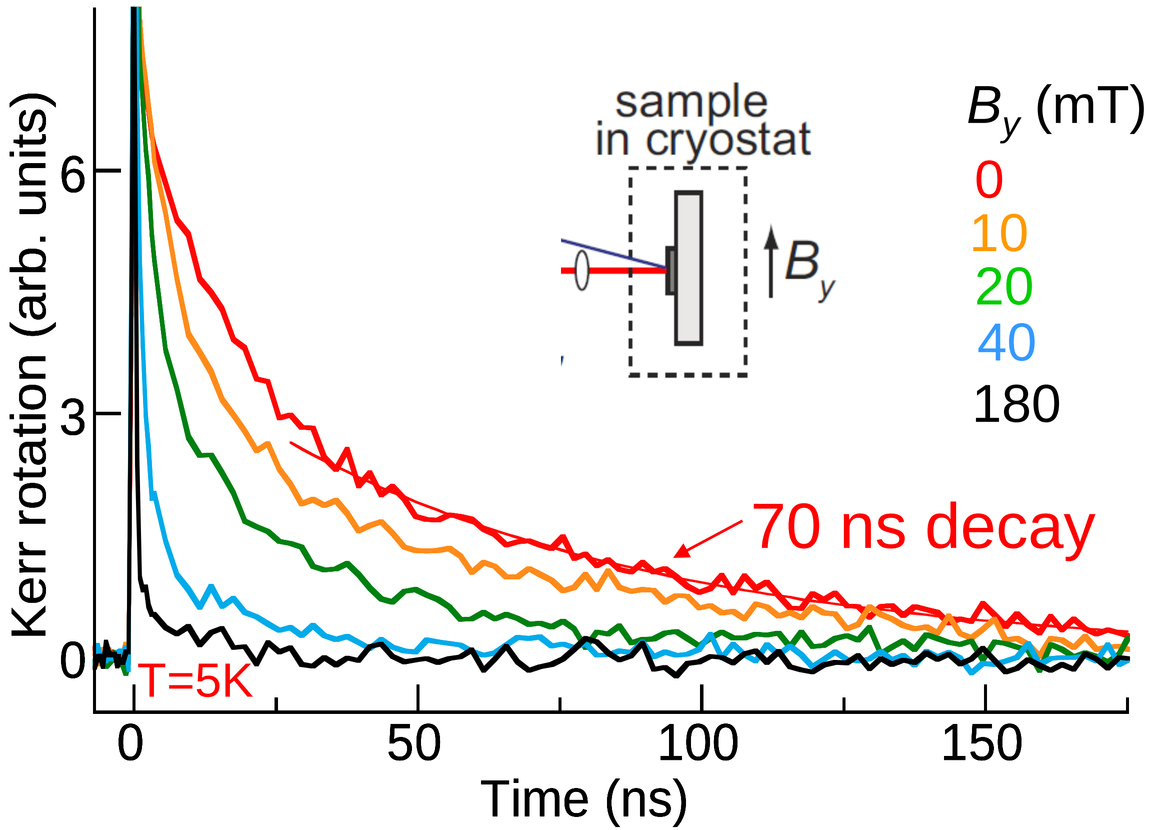
Important modifications:

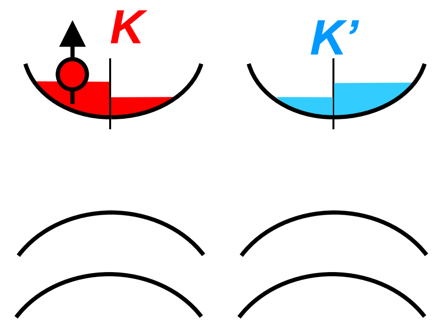
- Pulse Picker (to reduce Ti:S repetition rate)
- Electronic Delay Generator (to achieve arbitrary time delays)

Allows direct access to microsecond-long pump-probe delays

Electron-doped (*n*-type) regime:

- 70 ns decay at B_y=0
- small B_y: much faster decay (spin effect)



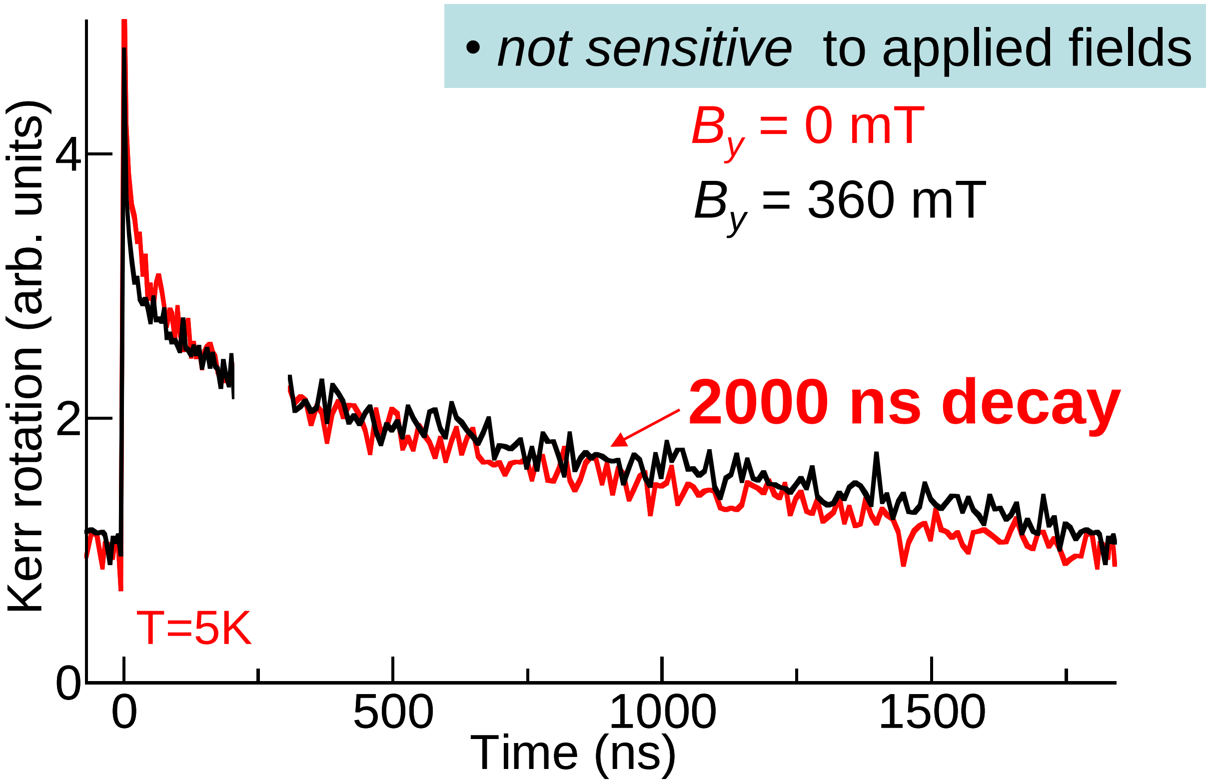


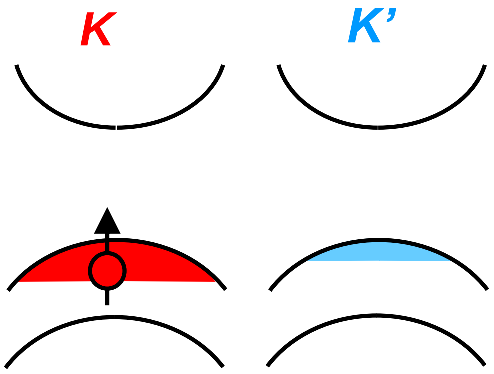
P. Dey *et al.*, PRL **119**, 137401 (2017)

Hole-doped (*p*-type) regime:

• *Extremely* long 2 microsecond polarization decay of holes at B_y=0

P. Dey *et al.*, PRL **119**, 137401 (2017)





• Consistent with spin-valley locking in valence band
• Suggests holes for exceptionally robust spin/valley polarization storage

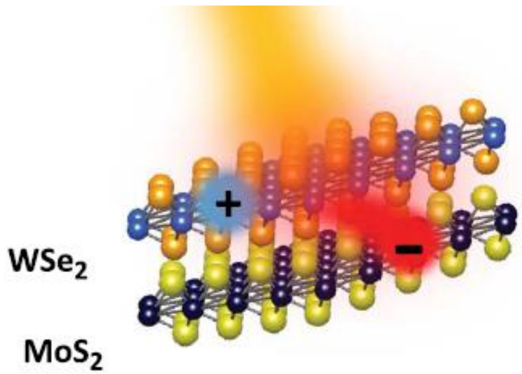
Also… J. Kim, F. Wang *et al.*, Sci. Adv. **3**, e1700518 (2017)

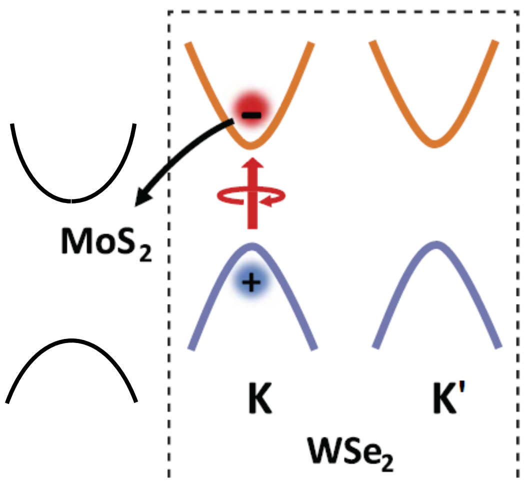
Also:

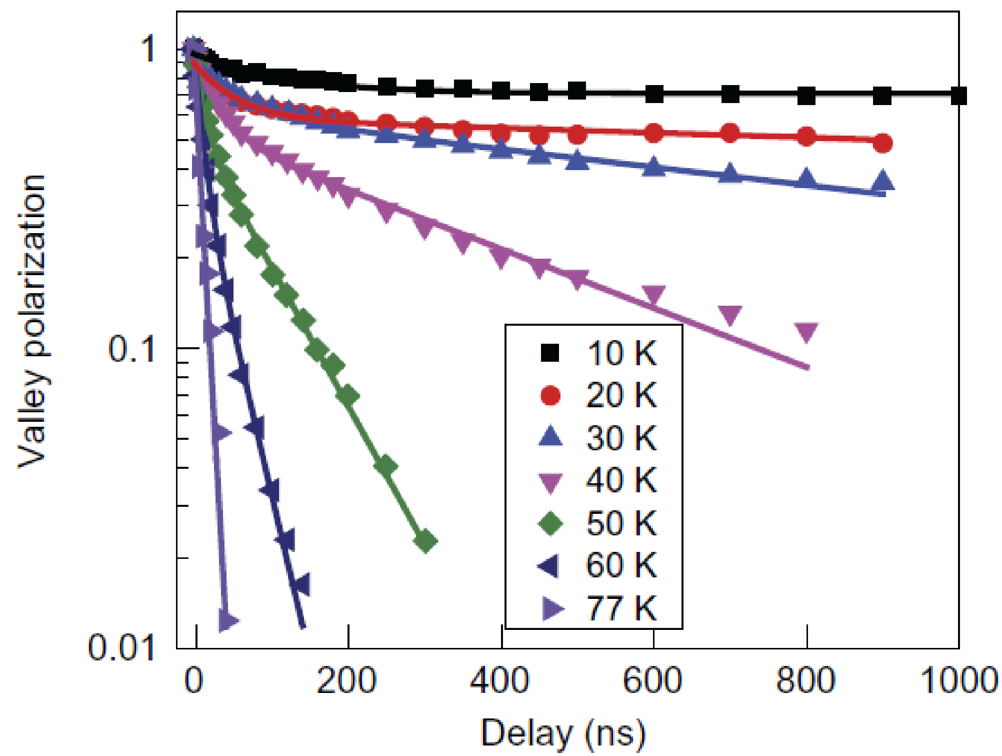
Observation of ultralong valley lifetime in WSe_2/MoS_2 heterostructures

Jonghwan Kim,[1,2*] Chenhao Jin,[1*] Bin Chen,[3] Hui Cai,[3] Tao Zhao,[1] Puiyee Lee,[1] Salman Kahn,[1] Kenji Watanabe,[4] Takashi Taniguchi,[4] Sefaattin Tongay,[3] Michael F. Crommie,[1,5,6] Feng Wang[1,5,6†]

Science Advances **3**, e1700518 (2017)

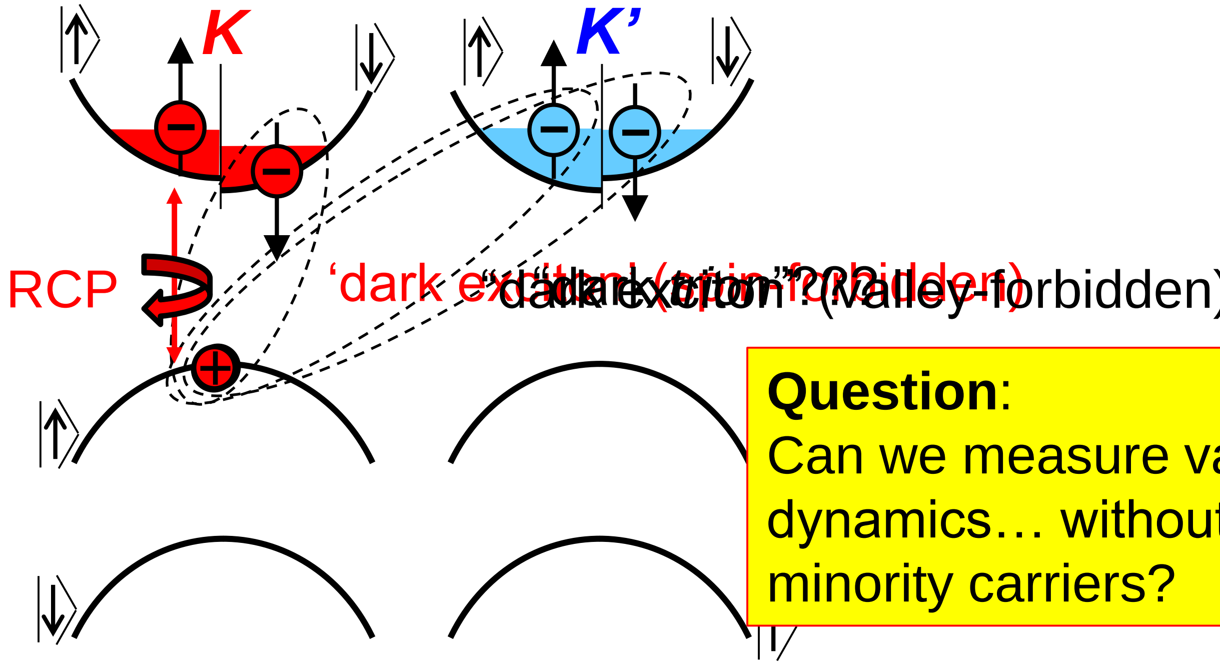






Lingering concerns: Pump-probe is *perturbative*

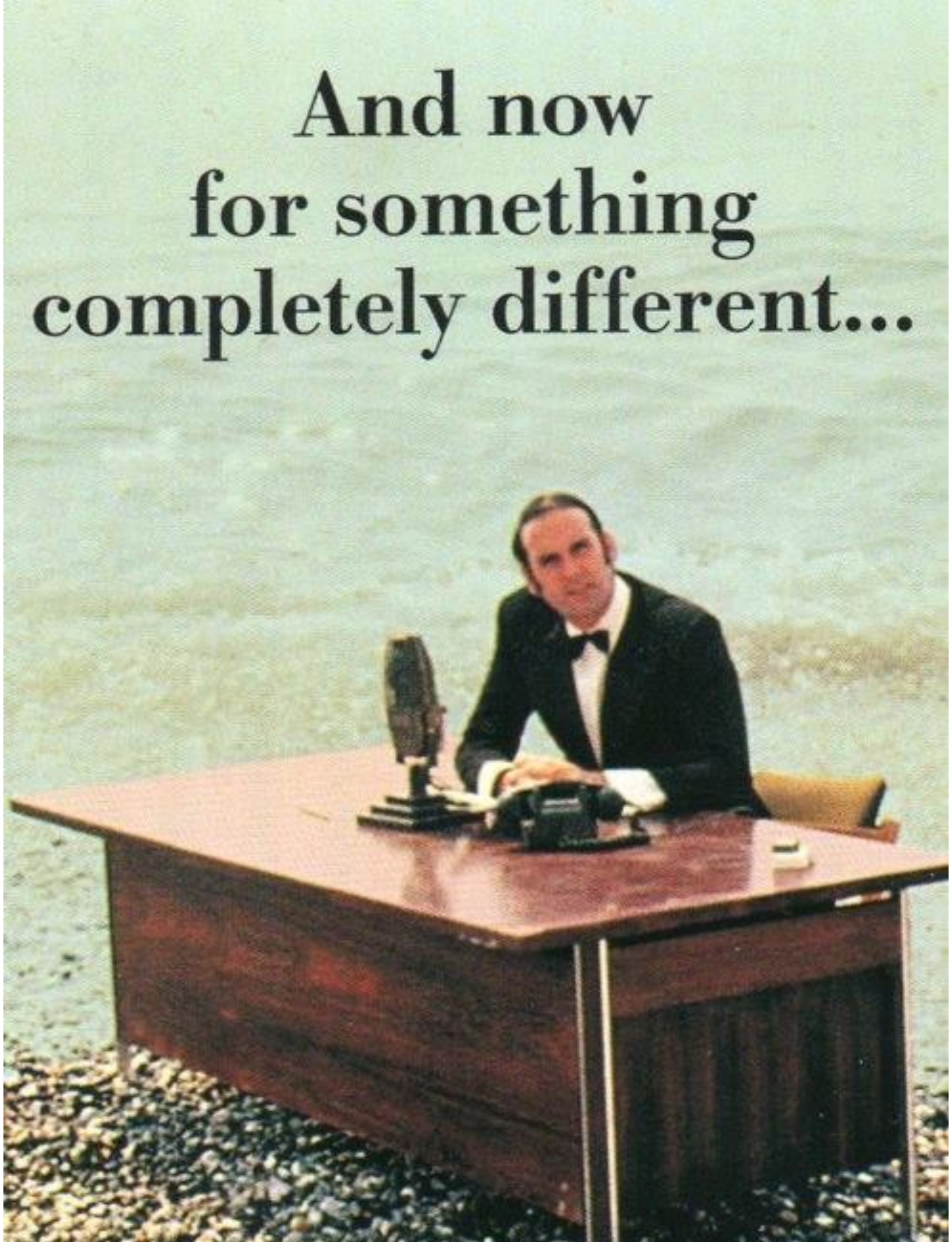
<u>Question</u>: role of (long-lived?) “dark” excitons & trions



Question:
Can we measure valley dynamics… without pumping minority carriers?

Evidence for “dark” (or at least “grey”) excitons:

Zhang, Heinz *et al.,* Nature Nano. **12**, 883 (2017)
Zhou *et al.,* Nature Nano. **12**, 856 (2017)
Molas *et al.*, 2D Materials **4**, 021003 (2017)
Wang et al., PRL **119**, 047401 (2017)

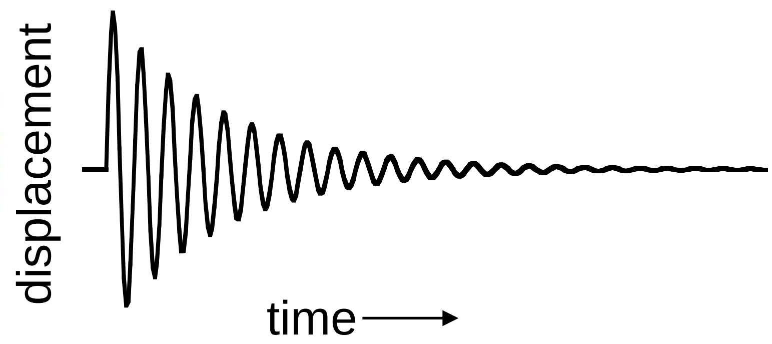


Question:
Can we measure valley dynamics… without pumping minority carriers?

“Noise spectroscopy”: a simple example
Simple mechanical system: Cantilever (diving board)

- What’s resonant frequency (ω_0)?
- What’s ringdown time (Q)?

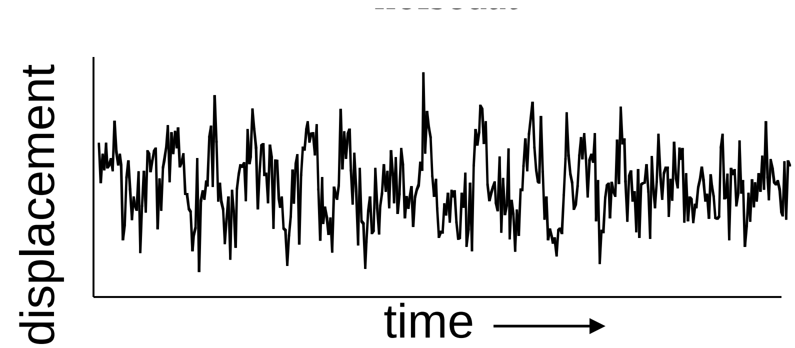
Method 1
Perturbative methods…
Measure dissipative response



“Noise spectroscopy”: a simple example
Simple mechanical system: Cantilever (diving board)

- What’s resonant frequency (ω_0)?
- What’s ringdown time (Q)?

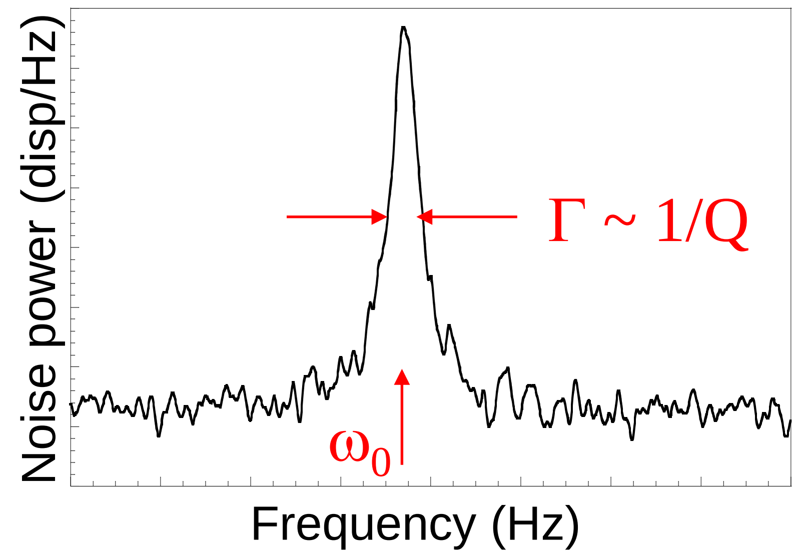
Method 2
“Listen” carefully to intrinsic thermal fluctuations (vibration noise)
Measure <δx(0) δx(t)>



"Noise spectroscopy": a simple example
Simple mechanical system: Cantilever (diving board)

Method 2
"Listen" carefully to intrinsic thermal fluctuations (vibration noise)
Measure <δx(0) δx(t)>

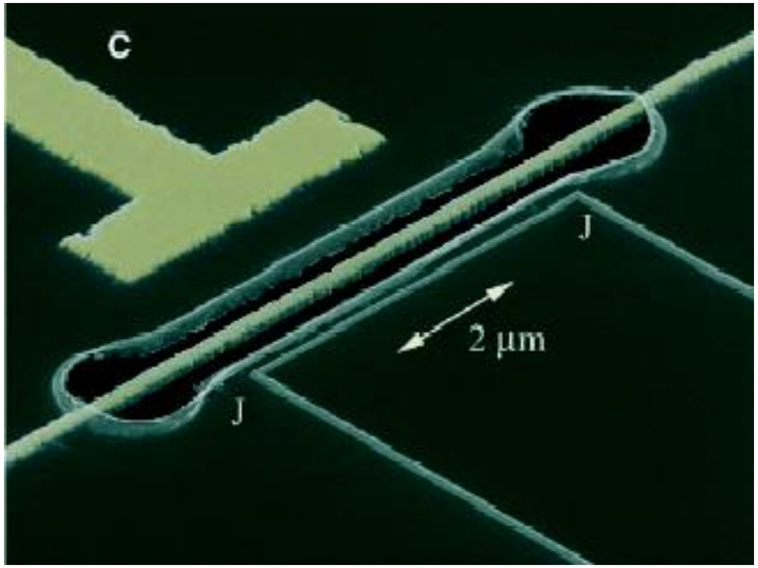
- What's resonant frequency (ω_0)?
- What's ringdown time (Q)?

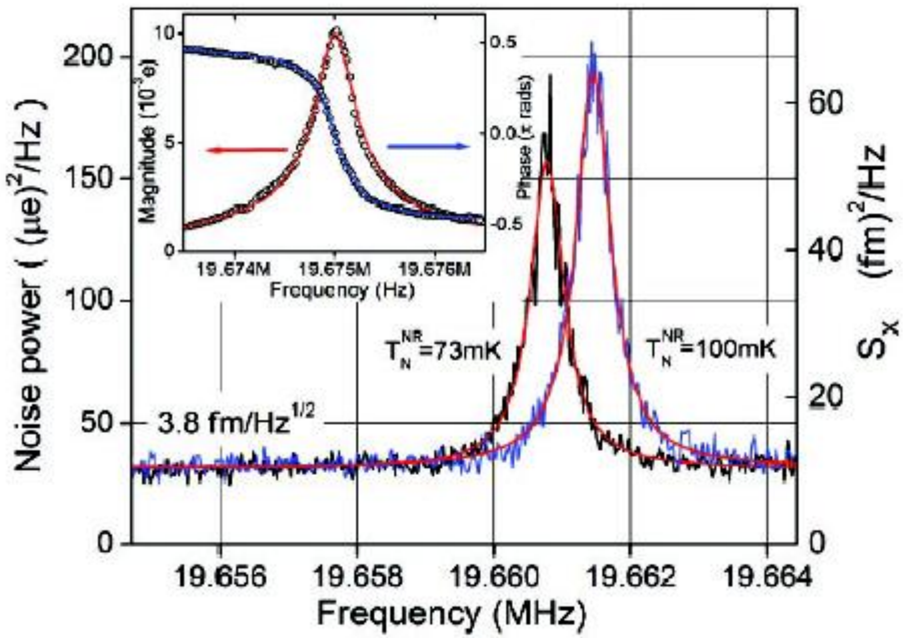


Fluctuation-Dissipation Theorem:
'Spectrum of fluctuations completely describes the driven response'

Nanometer-scale diving board (mechanical resonator)

K. Schwab (Science, 2004)

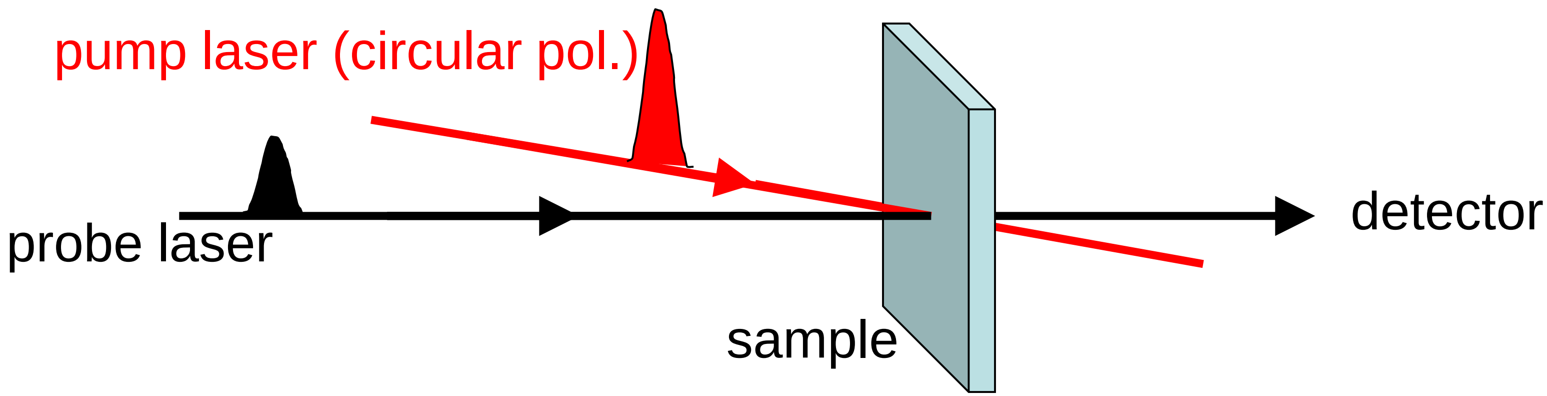




** Noise signatures become an increasing fraction of "driven" signal as things get small **

Magnetic analogy: stochastic ‘spin noise’

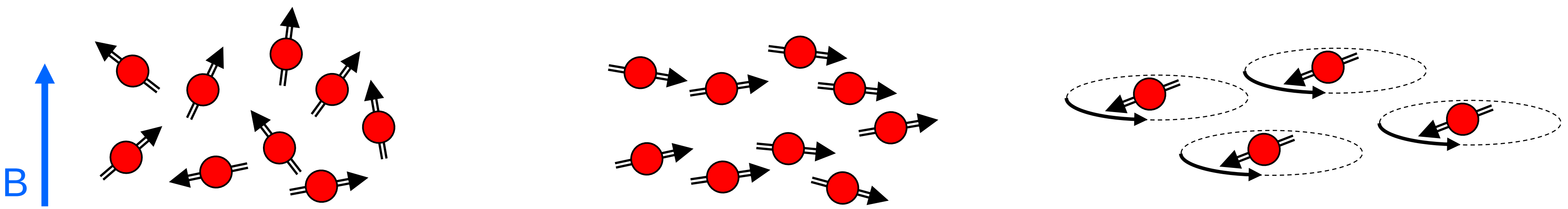
Normally, spin dynamics revealed with spin-resonance (NMR, ESR),pump-probe optics: techniques are necessarily perturbative



Start with spins in thermal equilibrium…

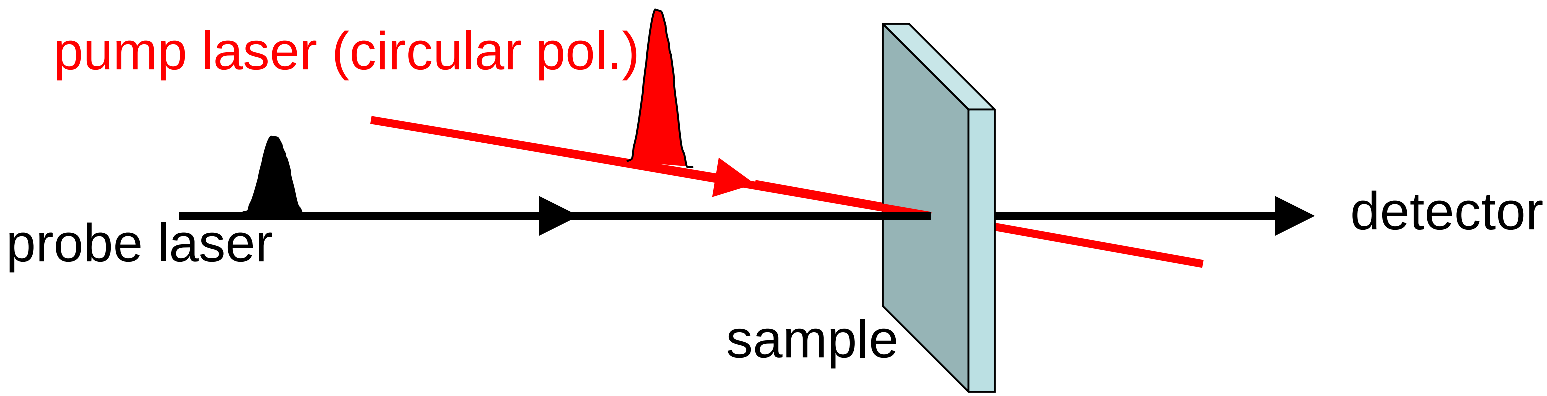
…then inject (or tip, or pump, etc…)

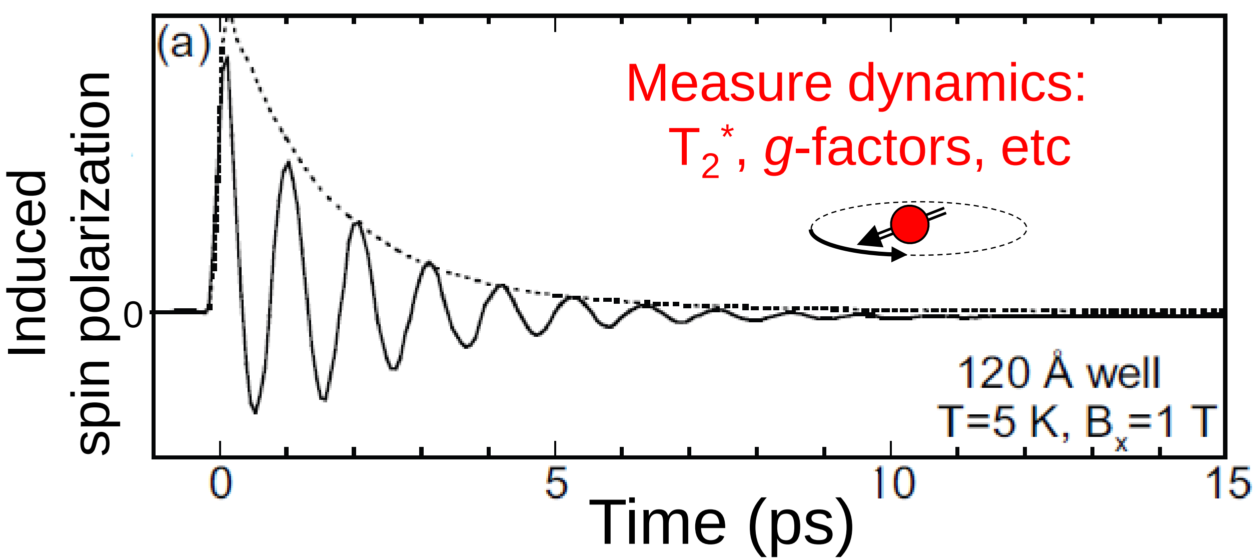
…then measure (dissipative) response



Magnetic analogy: stochastic ‘spin noise’

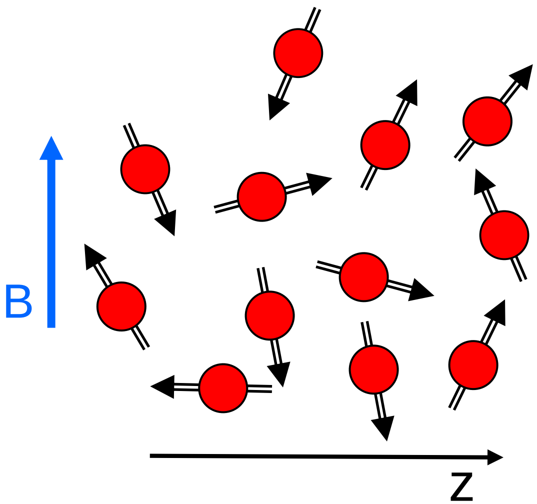
Normally, spin dynamics revealed with spin-resonance (NMR, ESR),pump-probe optics: techniques are necessarily perturbative



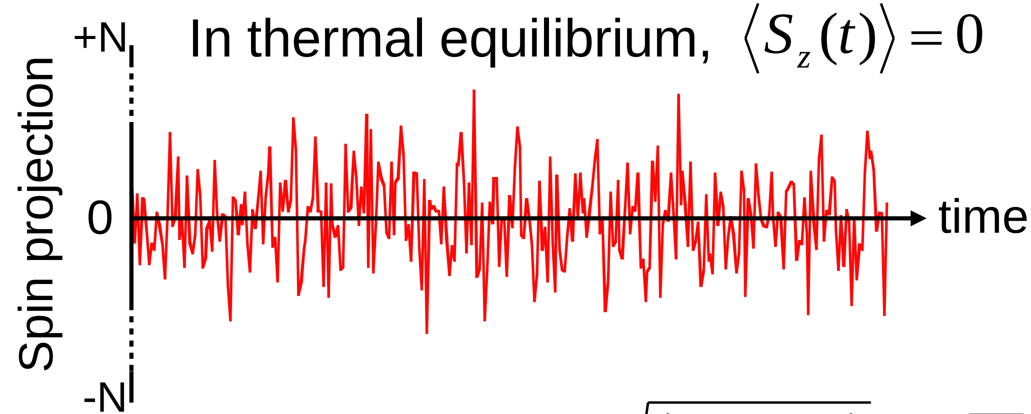


Dynamics *also* available via stochastic "spin noise"

Consider N uncorrelated spins in equilibrium…



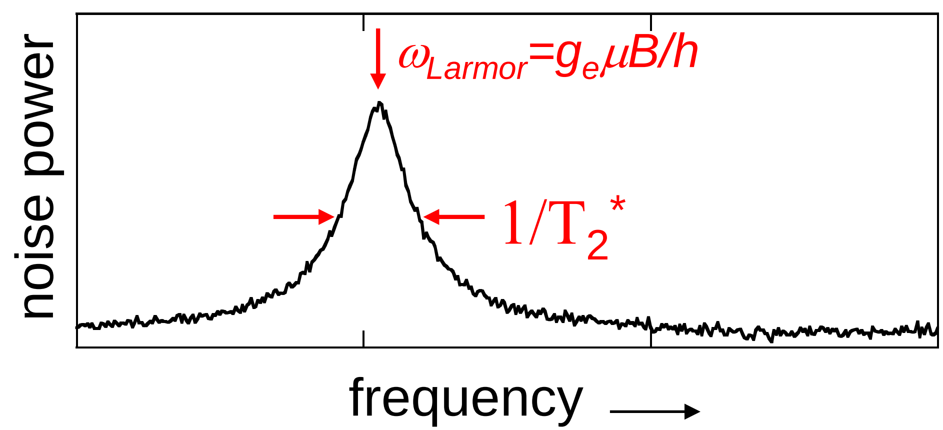
In thermal equilibrium, $\langle S_z(t) \rangle = 0$



But fluctuations exist: $\sqrt{\langle [S_z(t)]^2 \rangle} \sim \sqrt{N}$

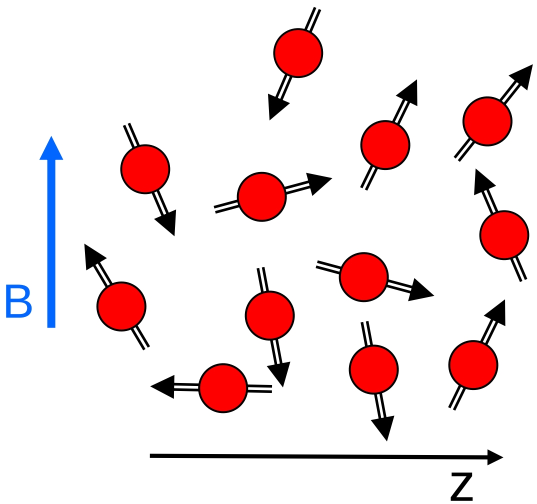
Correlation function: $\langle S_z(t) S_z(0) \rangle$

Spectrum of correlations:

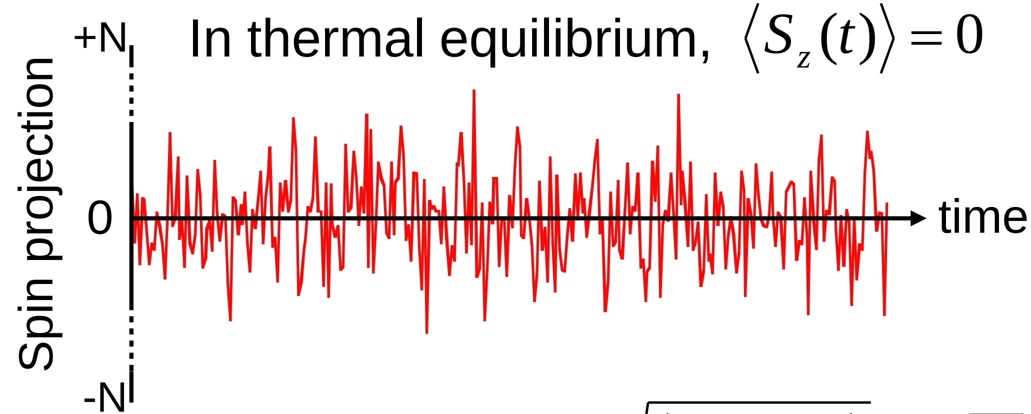


Dynamics *also* available via stochastic "spin noise"

Consider *N* uncorrelated spins in equilibrium…



In thermal equilibrium, $\langle S_z(t) \rangle = 0$



But fluctuations exist: $\sqrt{\langle [S_z(t)]^2 \rangle} \sim \sqrt{N}$

Correlation function: $\langle S_z(t) S_z(0) \rangle$

Fluctuation-dissipation theorem: $\chi''(\omega) \sim \int_{-\infty}^{\infty} \langle S_z(t) S_z(0) \rangle e^{-i\omega t} dt$

"Linear response of a system to external perturbation (ie, the susceptibility) can be described by the fluctuation properties of the system while in thermal equilibrium".

- *In principle: spin noise alone completely describes dynamics*

In 1946…

PHYSICAL REVIEW VOLUME 70, NUMBERS 7 AND 8 OCTOBER 1 AND 15, 1946

Nuclear Induction

F. Bloch
Stanford University, California
(Received July 19, 1946)

on page 2…

Even in the absence of any orientation by an external magnetic field one can expect in a sample with N nuclei of magnetic moment μ to find a resultant moment of the order $(N)^{\frac{1}{2}}\mu$ because of statistically incomplete cancellation. This moment, however, would naturally be very small

39 years later…

VOLUME 55, NUMBER 17 PHYSICAL REVIEW LETTERS 21 OCTOBER 1985

Nuclear-Spin Noise

Tycho Sleator and Erwin L. Hahn
Department of Physics, University of California, Berkeley, California 94720

and

Claude Hilbert and John Clarke
Department of Physics, University of California, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

(Received 12 August 198‾)

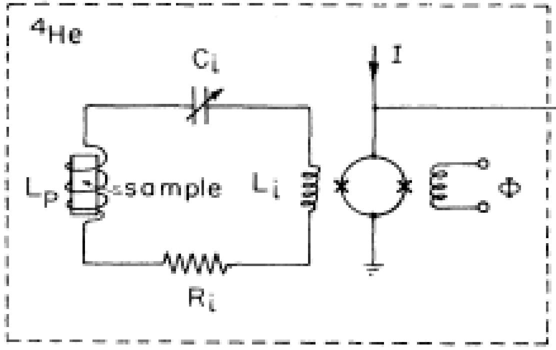


FIG. 1. Experimental configuration. Components in dashed box are immersed in liquid ^{4}He.

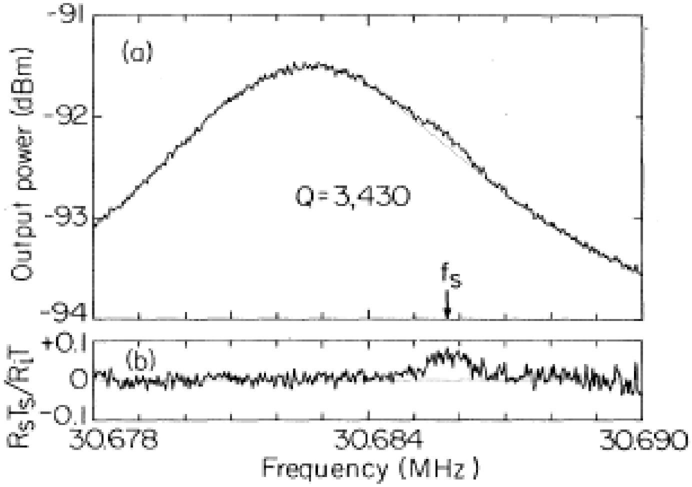


FIG. 3. Spectral density of (a) noise current for a $NaClO_3$ sample with saturated spins ($T_s = \infty$), and (b) nuclear-spin noise of $NaClO_3$ sample obtained from (a).

Nuclear spin noise imaging

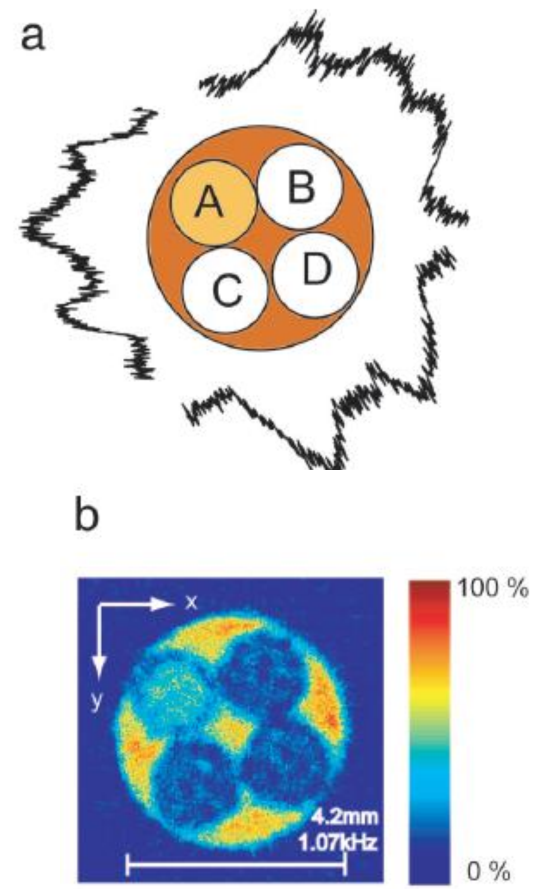
Proc. Nat. Acad. Sci. **103**, 6790 (2006)

Norbert Müller[†] and Alexej Jerschow[‡§]

[†]Institute of Organic Chemistry, Johannes Kepler University, Altenbergerstrasse 69, A-4040 Linz, Austria; and [‡]Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003

Communicated by E. L. Hahn, University of California, Berkeley, CA, March 9, 2006 (received for review December 7, 2005)

NMR images were obtained from the proton spin noise signals of a water-containing phantom, which was placed in the highly tuned, low-noise resonant circuit of a cryogenically cooled NMR probe in the presence of systematically varied magnetic field gradients. The spatially resolved proton spin density was obtained from the raw signal by a modified projection–reconstruction protocol. Although spin noise imaging is inherently less sensitive than conventional magnetic resonance imaging, it affords an entirely noninvasive visualization of the interior of opaque objects or subjects. Thus, tomography becomes possible even when neither x-ray nor radio frequency radiation can be applied for technical or safety reasons.



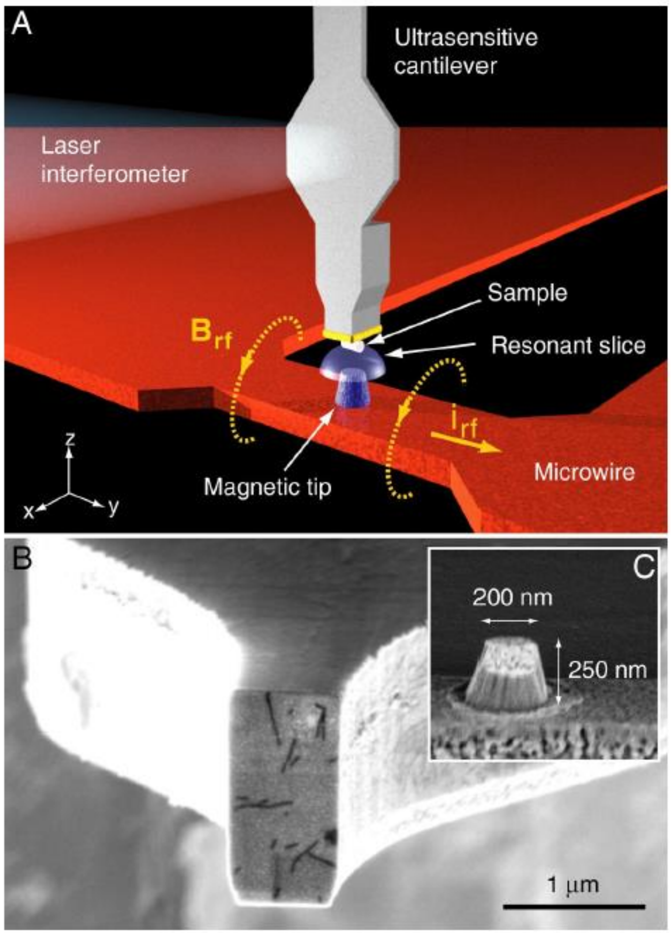
Nanoscale magnetic resonance imaging

PNAS 106, 1313 (2009)

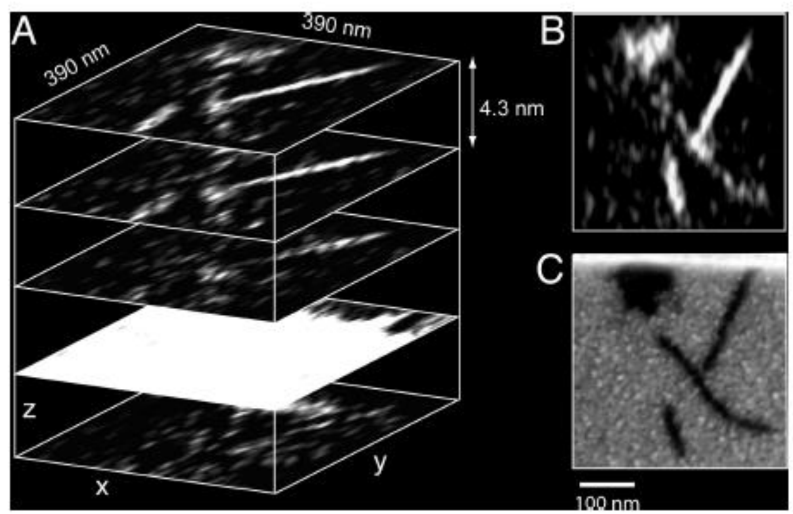
C. L. Degen[a], M. Poggio[a,b], H. J. Mamin[a], C. T. Rettner[a], and D. Rugar[a,1]

[a]IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120; and [b]Center for Probing the Nanoscale, Stanford University, 476 Lomita Mall, Stanford, CA 94305

Communicated by Stuart S. P. Parkin, IBM Almaden Research Center, San Jose, CA, December 1, 2008 (received for review August 21, 2008)

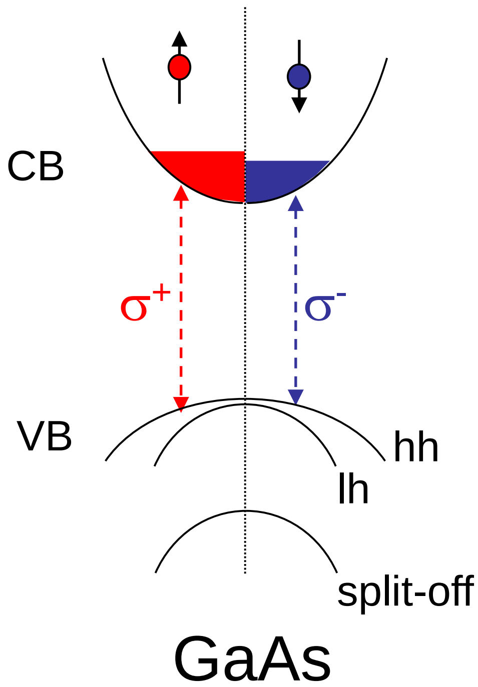


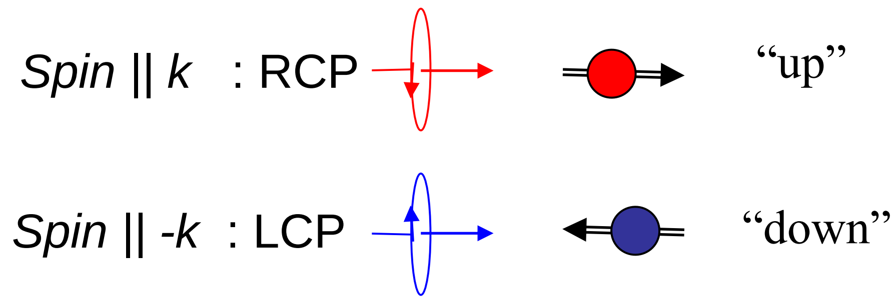
The spin signal originates from the naturally occurring $\sqrt{N}$ statistical polarization of the spin ensemble ("spin noise"), where N is the number of ^{1}H spins in the measurement volume (19, 23, 31–33). Using the statistical polarization is advantageous because its root-mean-square amplitude exceeds the mean Boltzmann polarization for nanoscale volumes of spins (23).

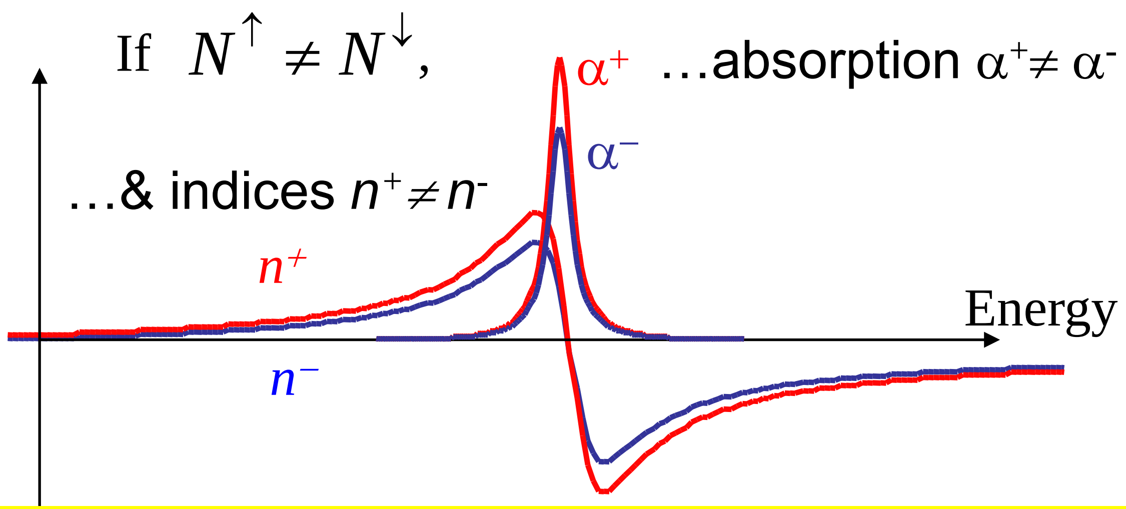


Passive detection of spin/valley noise using optical Faraday rotation

- *Possible when σ^+/σ^- optical selection rules exist due to spin-orbit coupling eg, spin up/down in III-V semiconductors… or K/K' valleys in TMD monolayers*



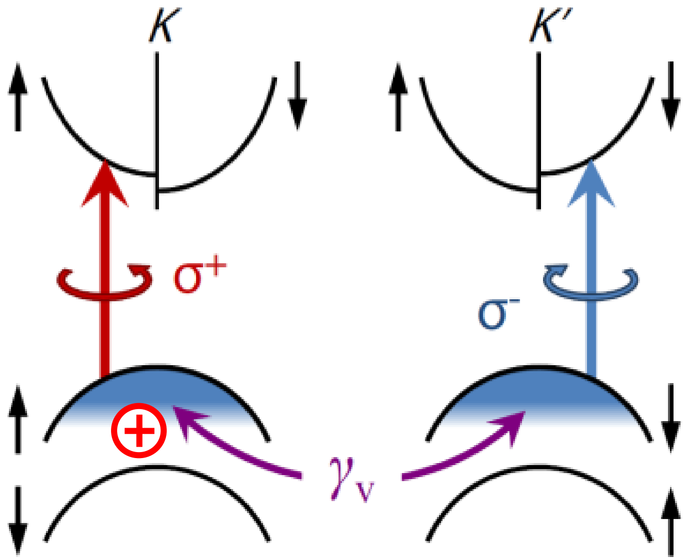


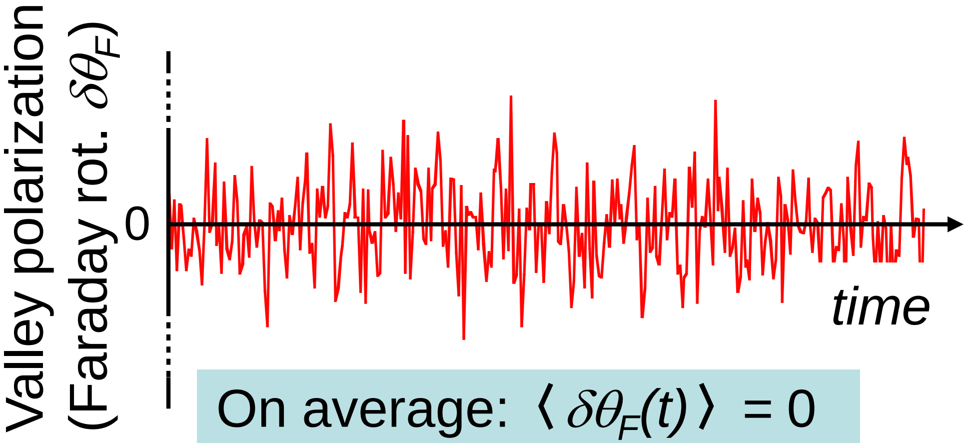


Faraday rotation: $\theta_F(t) \propto n^+ - n^- \propto N^{\uparrow} - N^{\downarrow} \propto M_z(t)$
Probe laser can be tuned far from absorption, but still measure spin via $n^+ - n^-$
In this regard, it is "non-perturbing" probe

"Valley Noise Spectroscopy" in TMD monolayers

Consider Fermi sea of holes in thermal equilibrium…





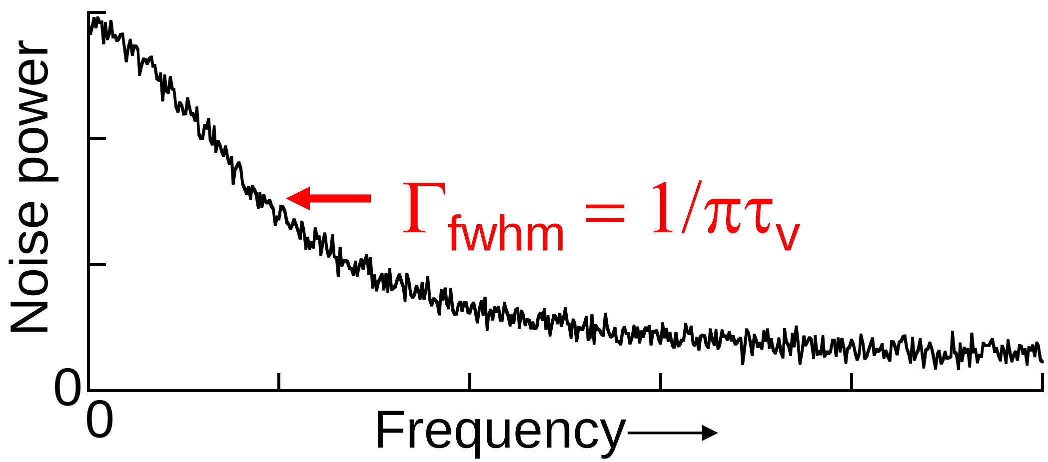
On average: $\langle \delta\theta_F(t) \rangle = 0$

But fluctuations exist: $\langle [\delta\theta_F(t)]^2 \rangle \neq 0$

Valley correlation function: $\langle \delta\theta_F(t)\, \delta\theta_F(0) \rangle$

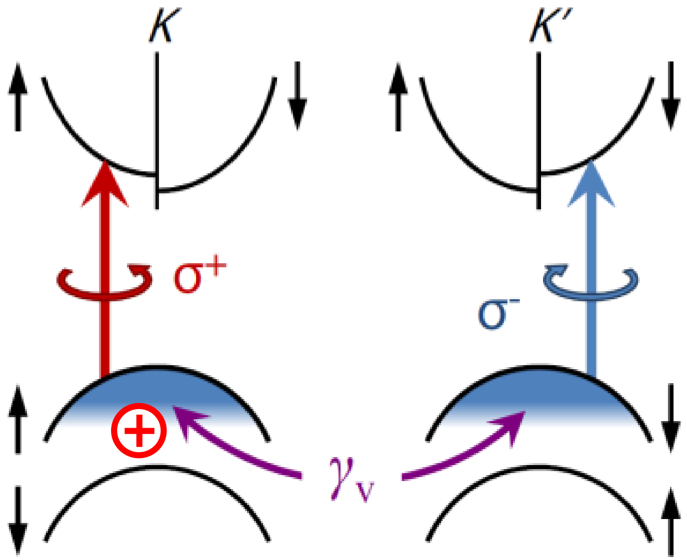
Spectrum of correlations: "Valley Noise"

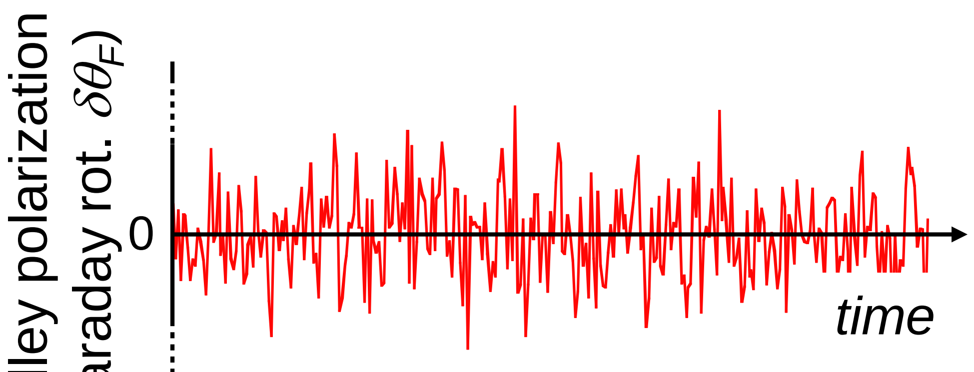
- *Width* gives timescales
- *Shape* gives mechanism
  etc…



"Valley Noise Spectroscopy"

Consider Fermi sea of holes in thermal equilibrium…





On average: $\langle \delta\theta_F(t) \rangle = 0$

But fluctuations exist: $\langle [\delta\theta_F(t)]^2 \rangle \neq 0$

Valley correlation function: $\langle \delta\theta_F(t)\, \delta\theta_F(0) \rangle$

Fluctuation-Dissipation Theorem: $\chi''(\omega)$ = FFT [$\langle \delta\theta_F(t)\, \delta\theta_F(0) \rangle$]

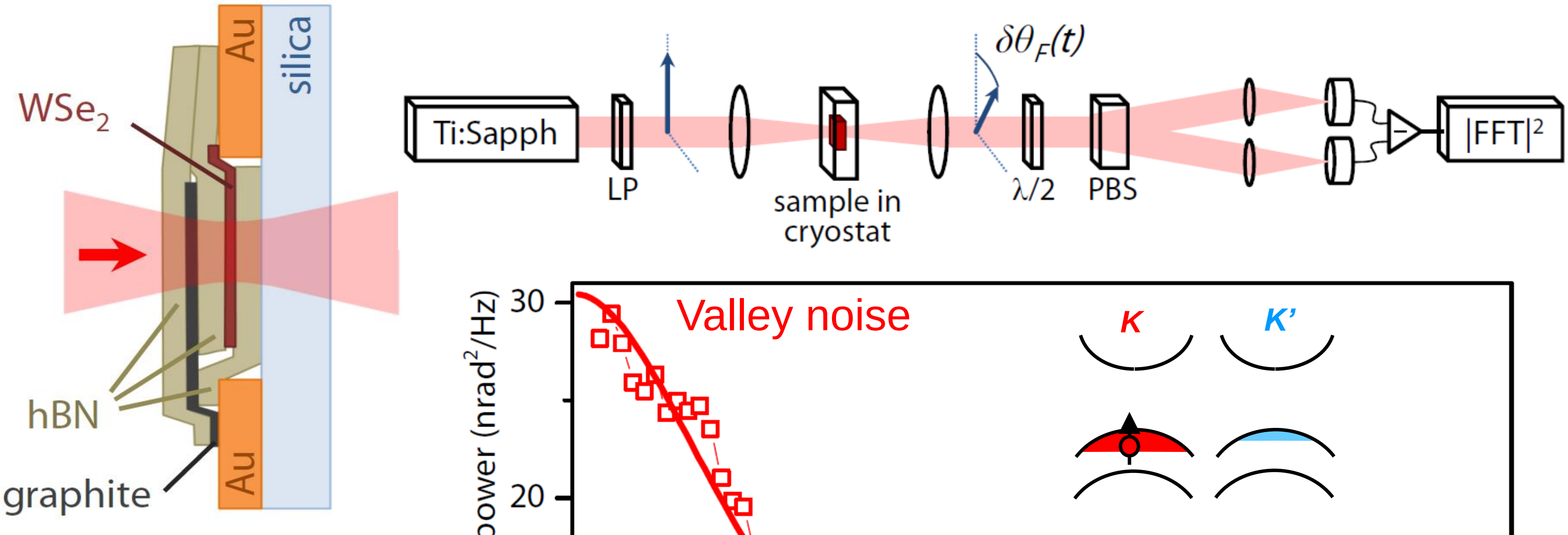
"Linear response of a system to external perturbation (ie, the susceptibility) can be described by the fluctuation properties of the system <u>while in thermal equilibrium</u>".

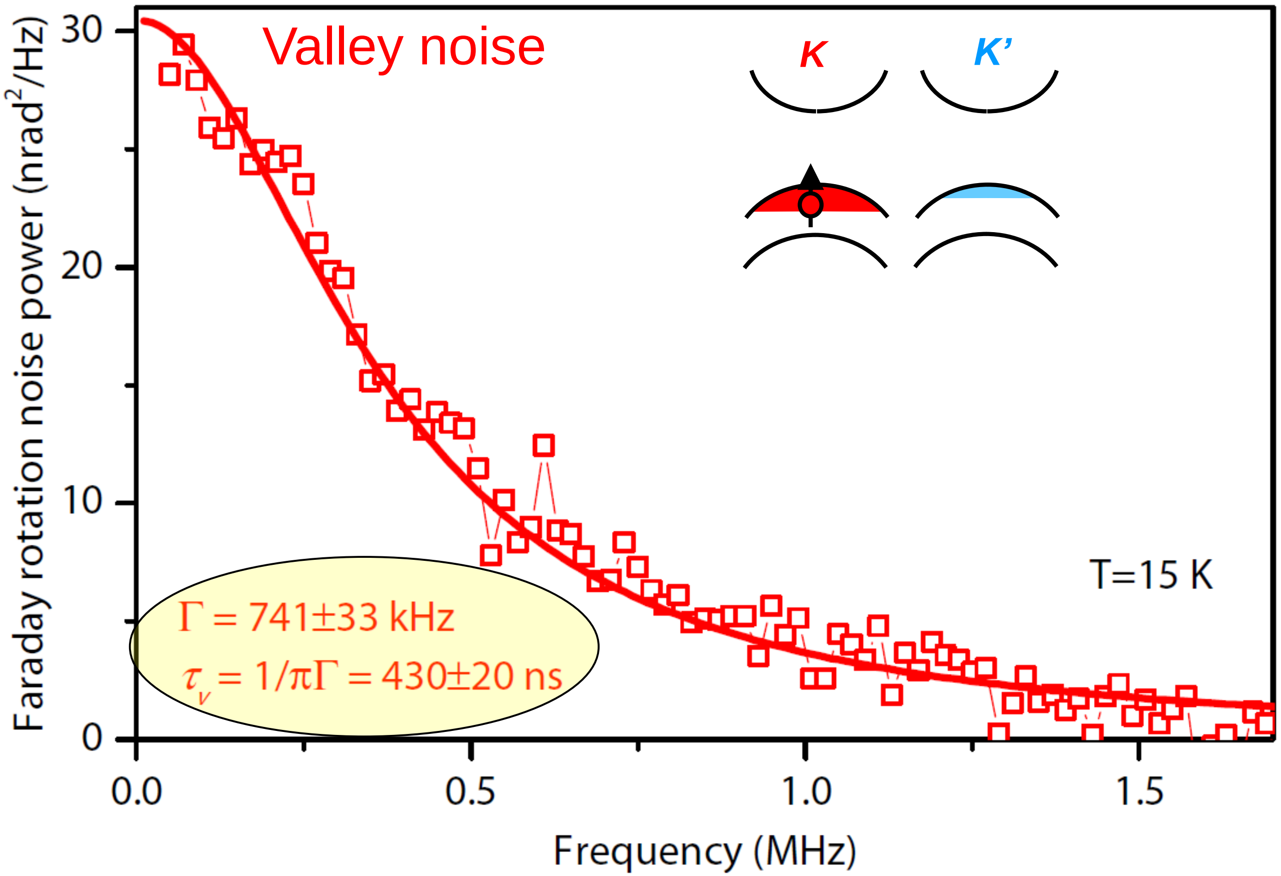
- *In principle: valley noise alone describes valley dynamics*

No perturbation, drive, or excitation necessary

M. Goryca *et al.* Sci. Adv. 5, eaau4899 (2018)

"Listening" to valley noise of holes in monolayer WSe_2

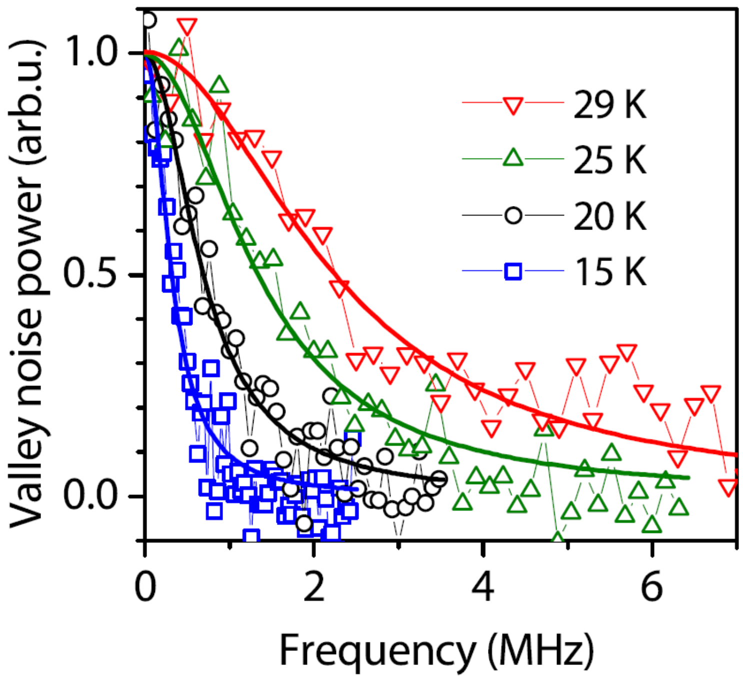


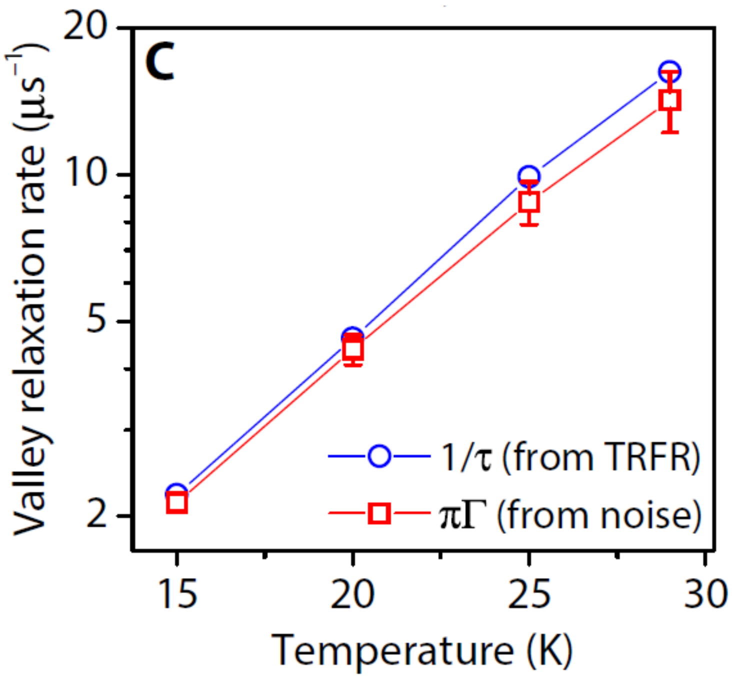


Nathan Wilson
(U Washington)

M. Goryca *et al.* Sci. Adv. 5, eaau4899 (2018)

Temperature-dependent valley relaxation of holes



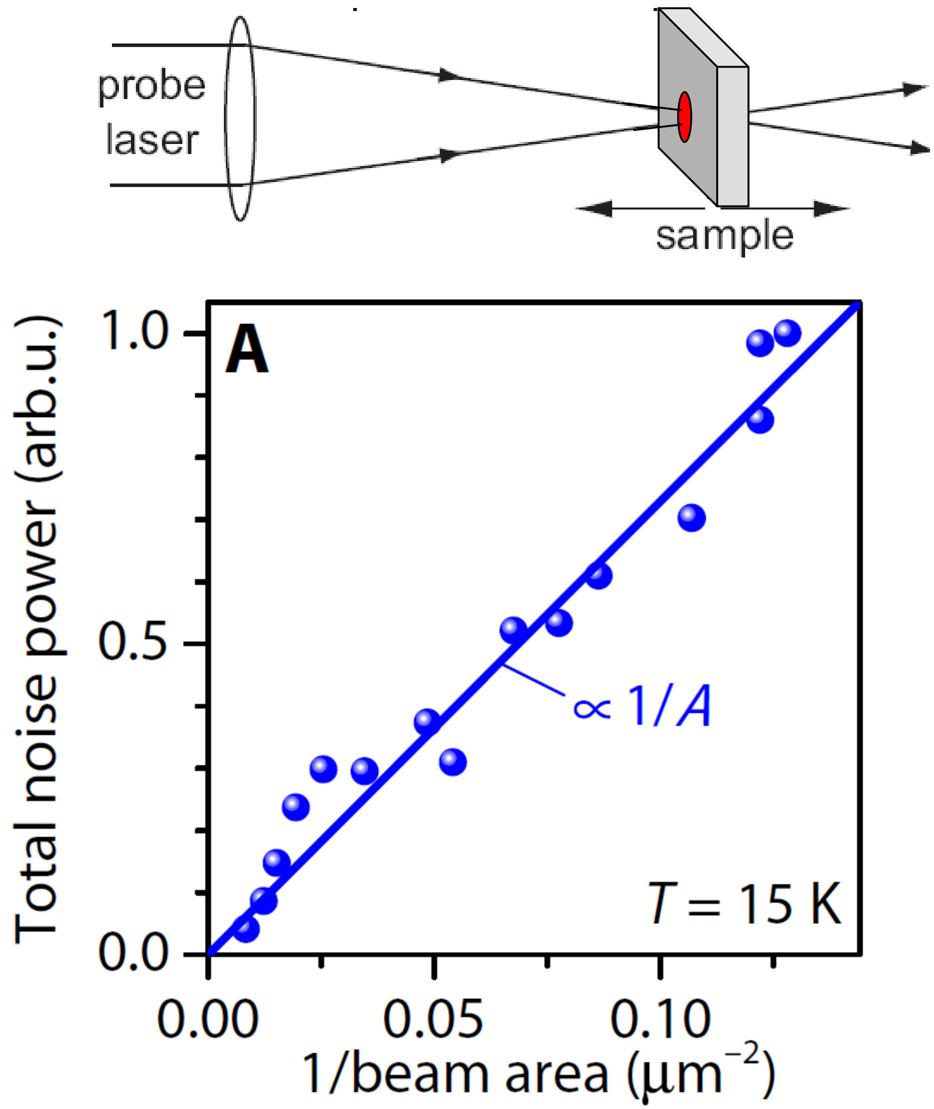


Theory:
Ochoa, Fal'ko, PRB (2014)
Yu & Wu, PRB (2014)
Song& Dery, PRL (2013)
Kormanyos, 2D Mater (2015)

M. Goryca *et al.* Sci. Adv. 5, eaau4899 (2018)

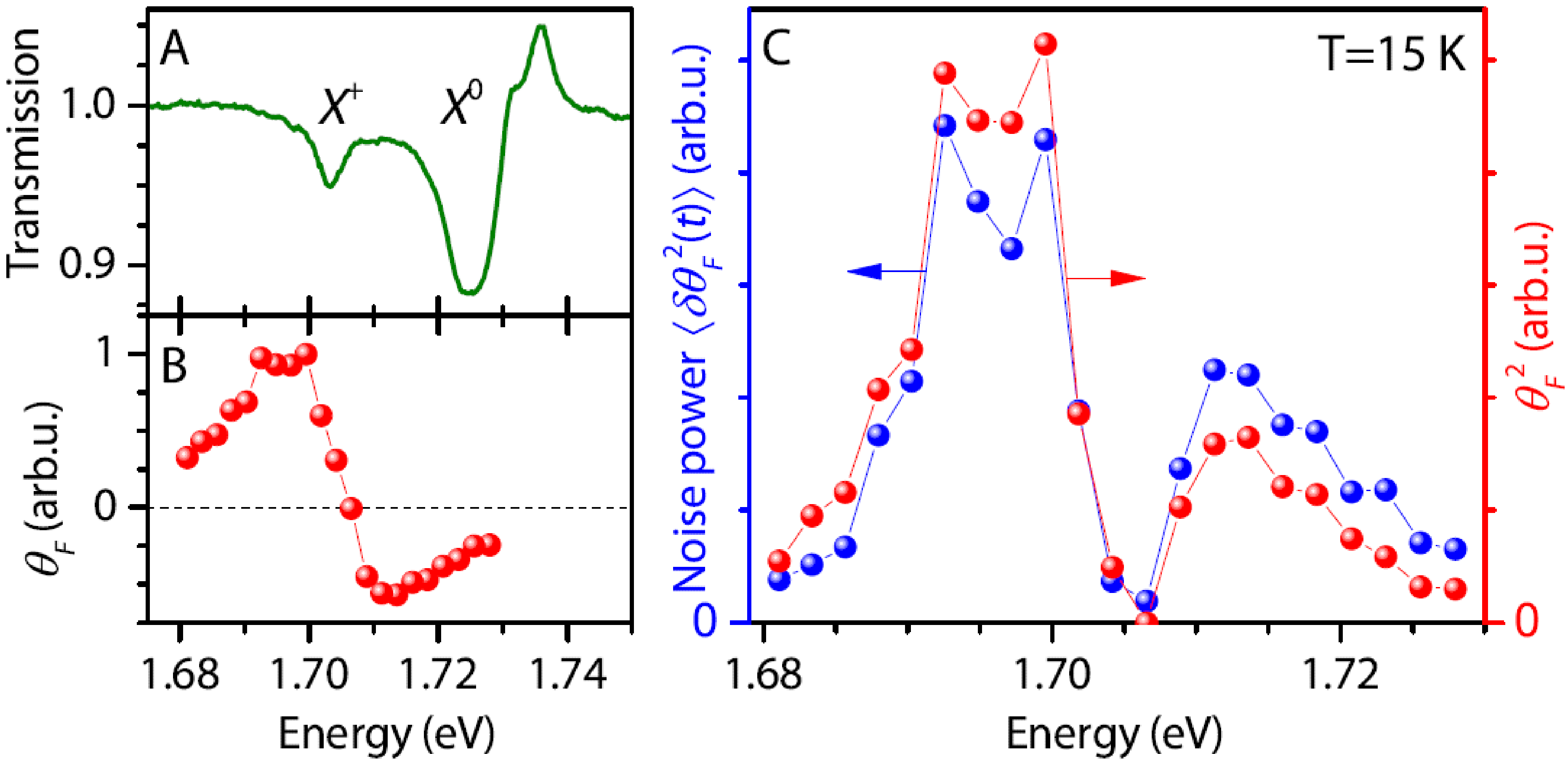
Inverse scaling with probed area – *fewer* holes give *more* noise

Noise signal is a *larger* fraction of saturated signal when probing *fewer* holes.



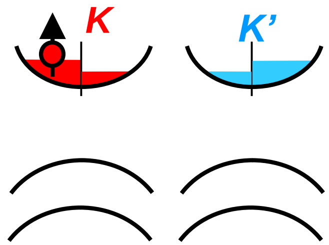
M. Goryca *et al.* Sci. Adv. 5, eaau4899 (2018)

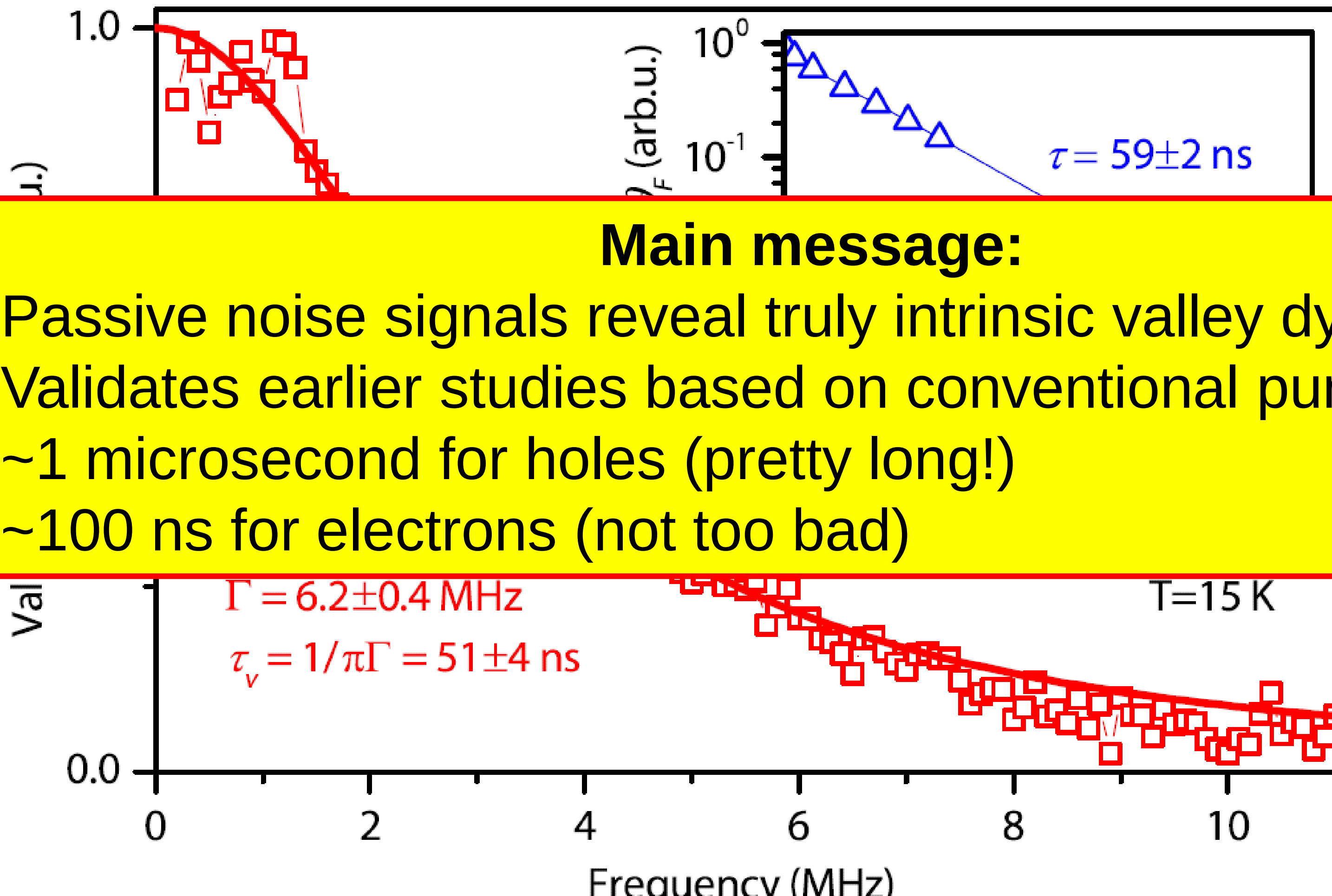
Spectral dependence of valley noise



M. Goryca *et al.* Sci. Adv. 5, eaau4899 (2018)

Electron valley noise in *n*-type monolayer WSe_2





Main message:

Passive noise signals reveal truly intrinsic valley dynamics

Validates earlier studies based on conventional pump-probe

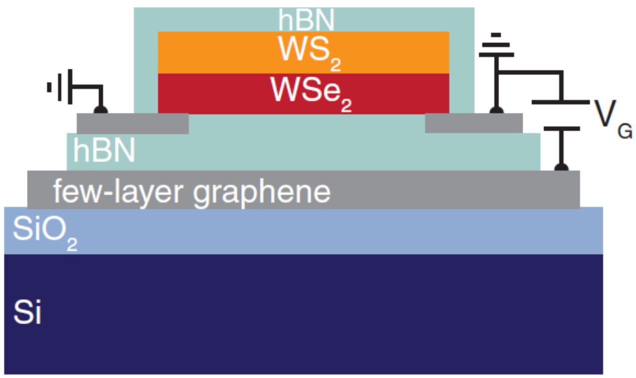
~1 microsecond for holes (pretty long!)

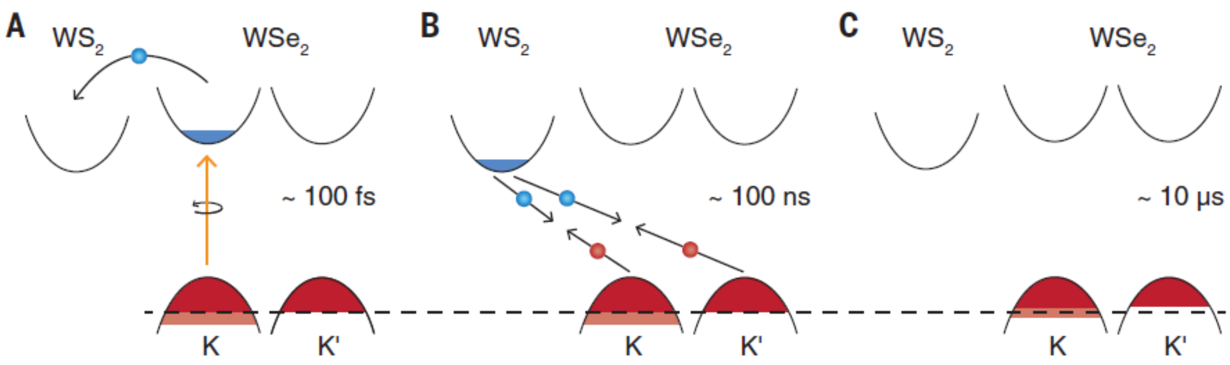
~100 ns for electrons (not too bad)

M. Goryca *et al.* Sci. Adv. 5, eaau4899 (2018)

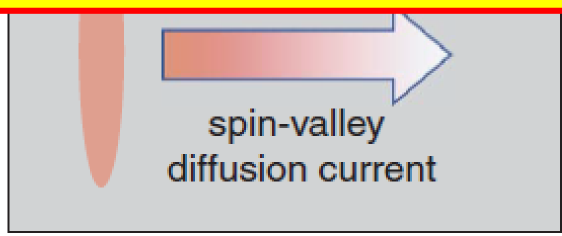
Imaging of pure spin-valley diffusion current in WS_2-WSe_2 heterostructures

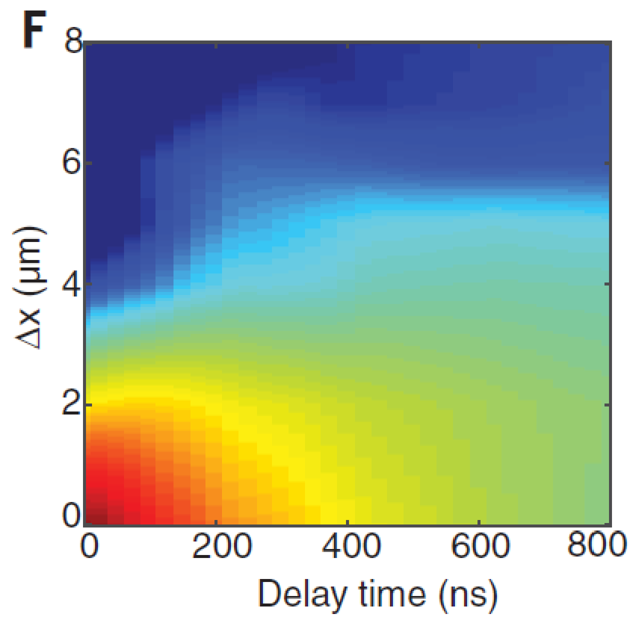
Jin *et al.*, *Science* **360**, 893–896 (2018)





- Tens of microseconds
- Tens of microns transport
- *(but still no K<->K' switching)*

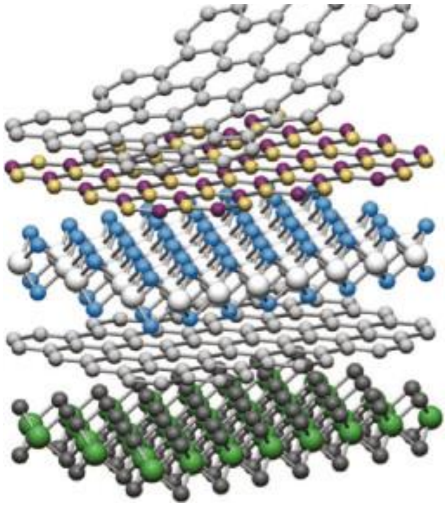


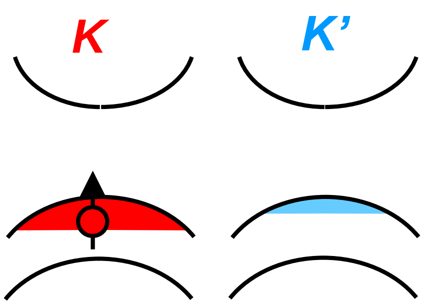


Summary

- **Valley dynamics in monolayer TMDs**
  - *Really short for excitons (~1ps)*
  - *Reasonably long for resident electrons and holes (but still only at low temperature)*

- **Thermodynamic "valley noise"**
  - *Nonperturbative access to intrinsic dynamics*
  - *Perhaps useful approach for quantum measurement*
  - *Validates recent pump-probe studies of carriers*





M. Goryca *et al,* Science Advances *5, eaau4899* (2018)
P. Dey *et al.*, PRL **119**, 137401 (2017)

Thank you!

NATIONAL HIGH MAGNETIC FIELD LABORATORY

Los Alamos NATIONAL LABORATORY