CCDM Tutorial
Optics of Layered Materials
31 July 2015

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Optics of Layered Materials Objectives

- Thickness of thin films can be determined:
  - Reflectance – optical penetration depths
  - Ellipsometry

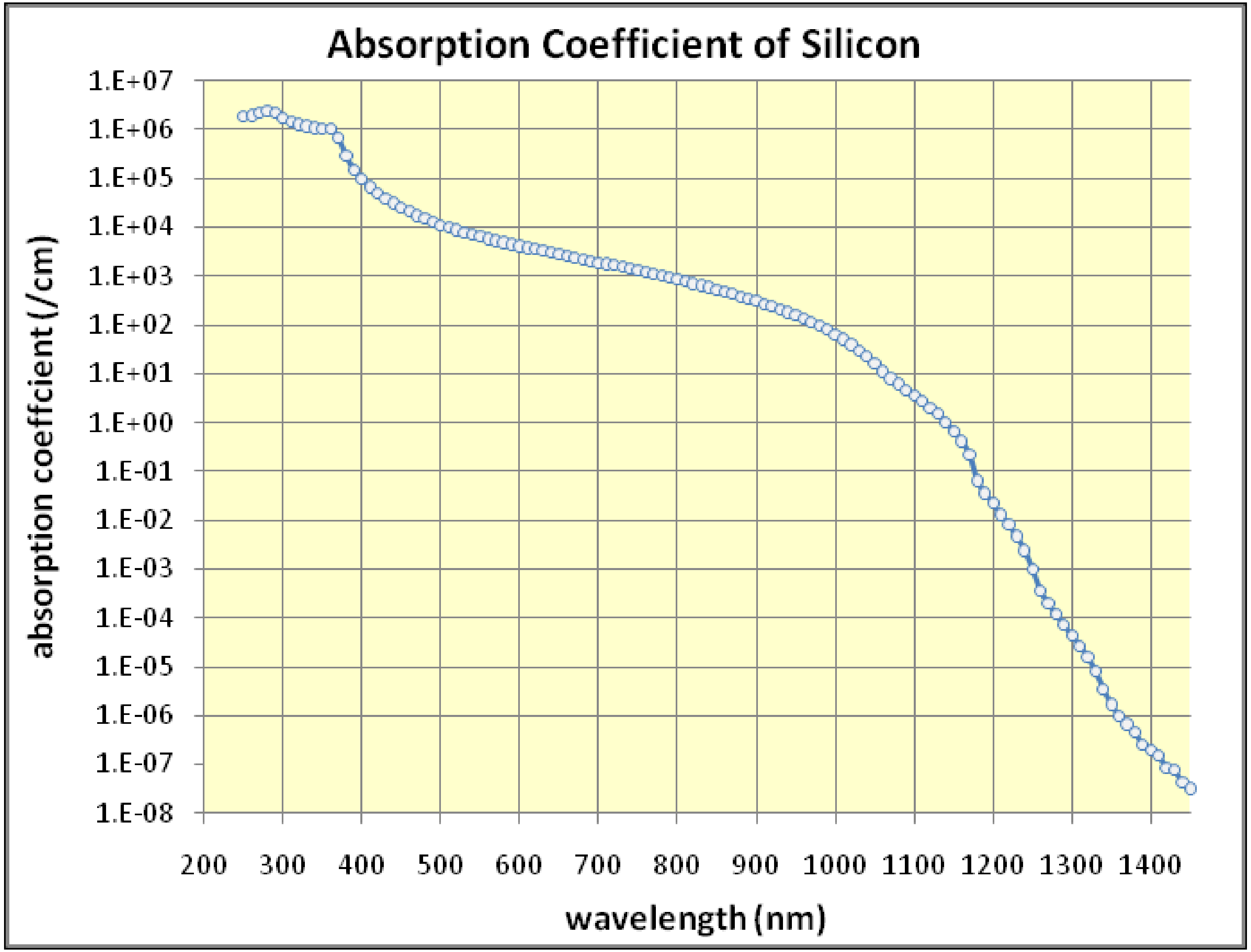
- Read band diagrams
  - Optics probes certain parts of the diagram
  - Recognize optical properties of direct and indirect bandgap

- Know which experimental technique to use to detect quasiparticles and measure their properties
  - Exciton/Biexciton/Trion luminescence/absorption
  - Time Evolution/Pump Probe
  - Phonon Raman

Incident Light

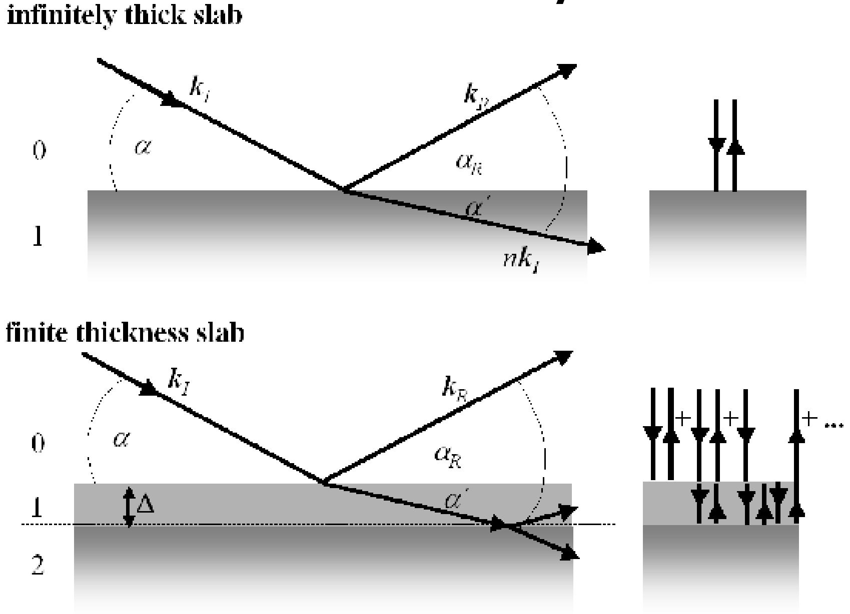
- Transmission
- Reflection
- Absorption

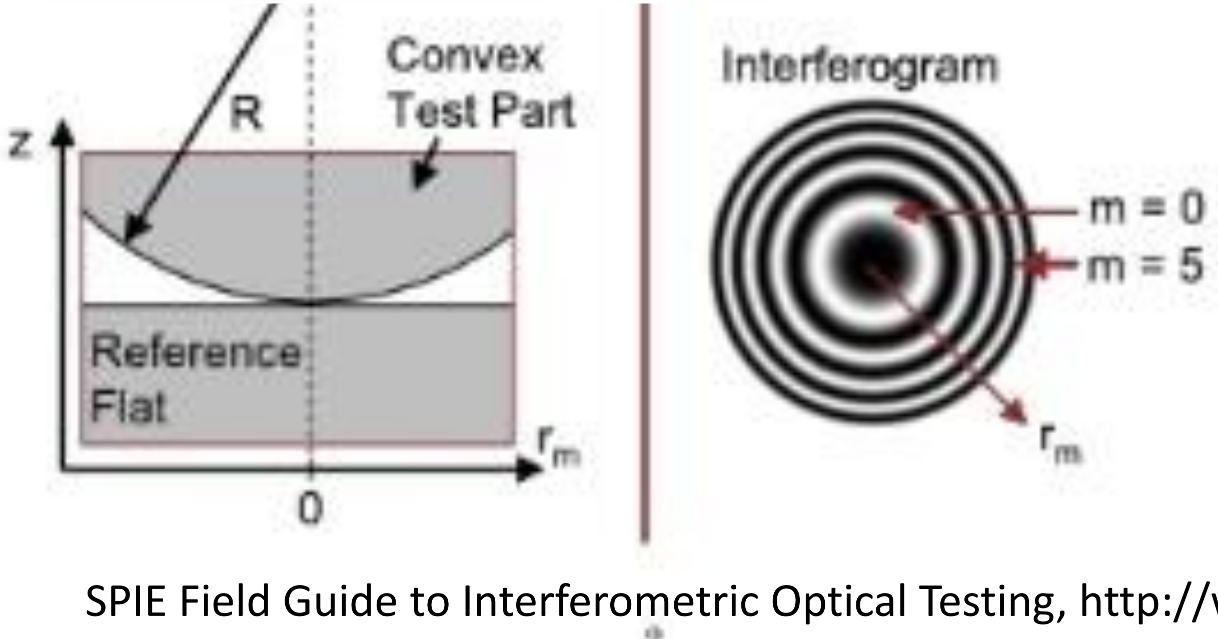
$$I(z)=I_0e^{-\alpha z}$$



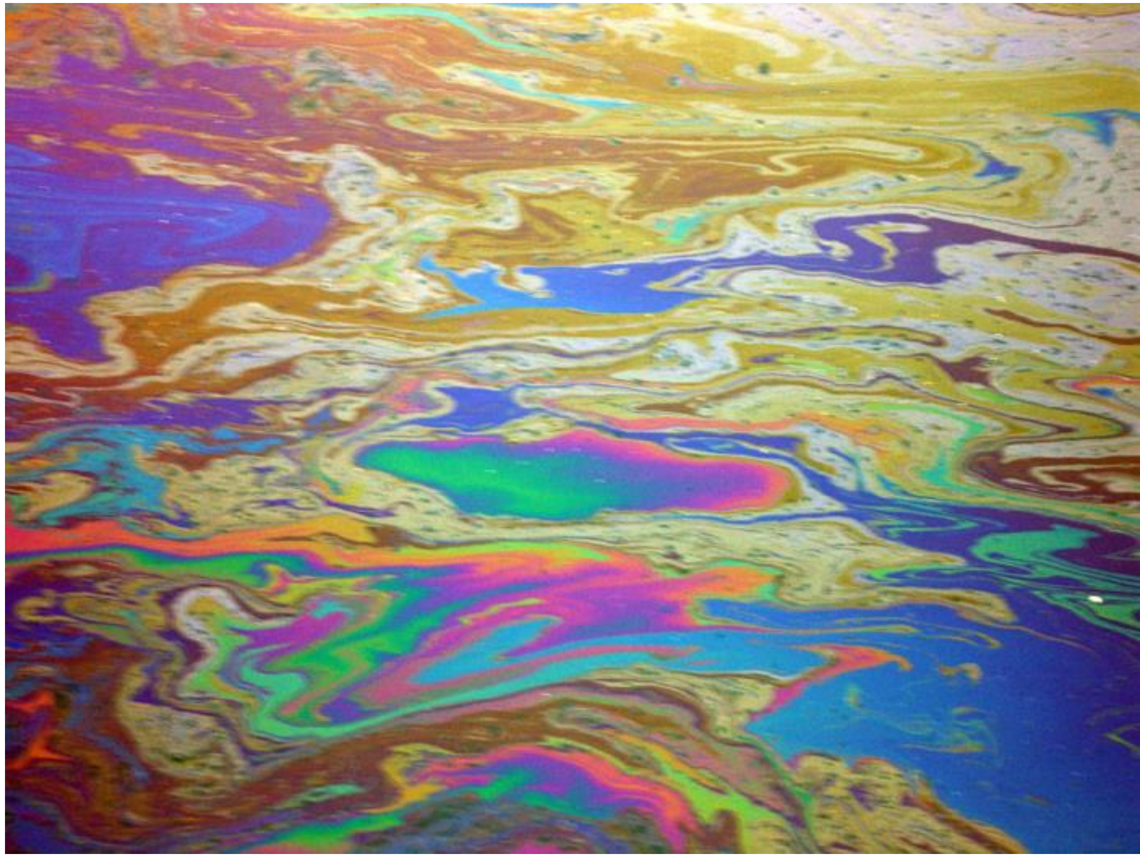
http://www.pveducation.org/pvcdrom/materials/optical-properties-of-silicon

Reflectivity: Newton's Fringes





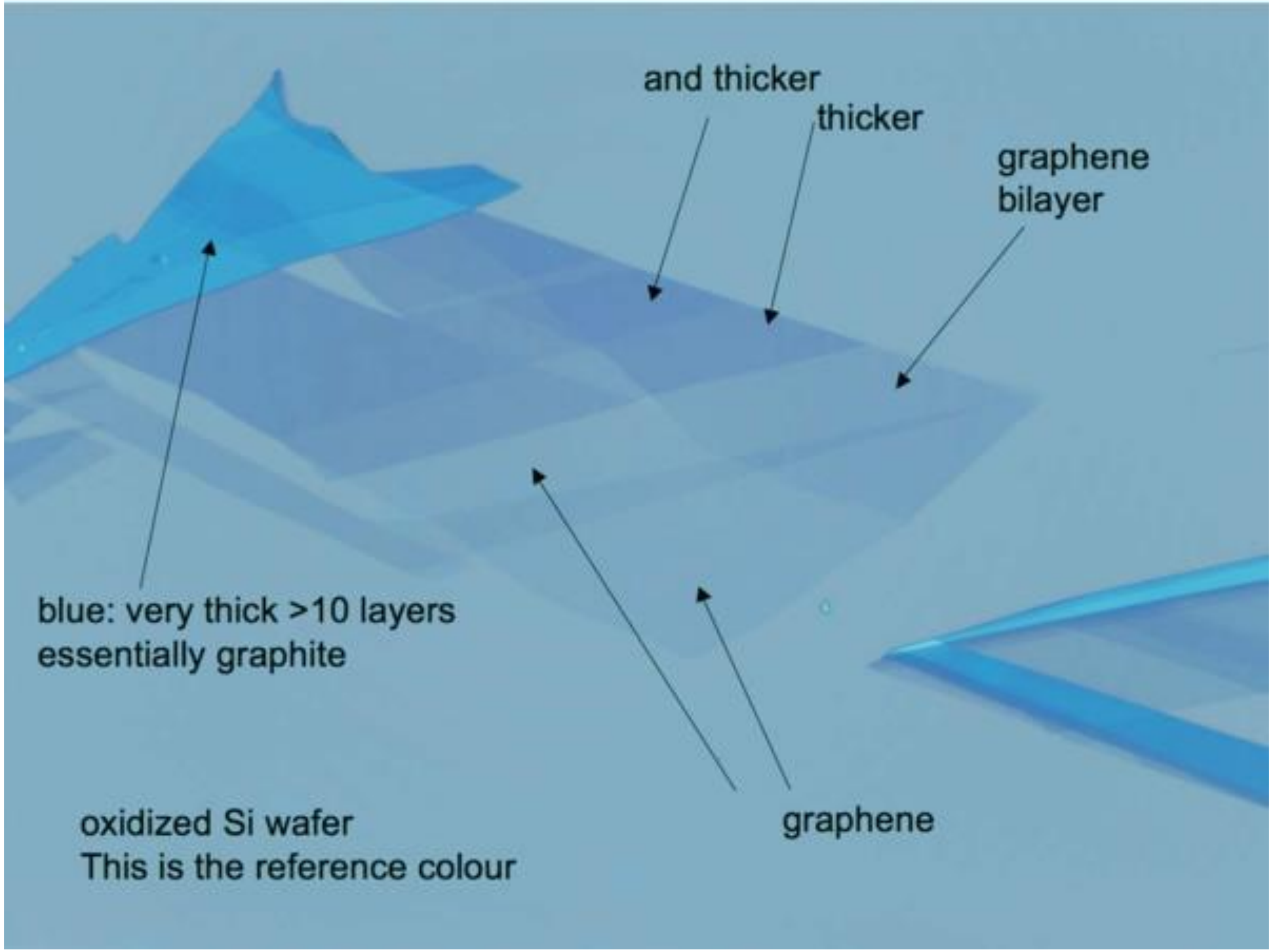
Can use the wave nature of light to determine thickness



http://www.whoi.edu/oilinocean

SPIE Field Guide to Interferometric Optical Testing, http://www.sladecek.org/NRS/node14.html

Differences in Reflectance Show Up in Single Layers

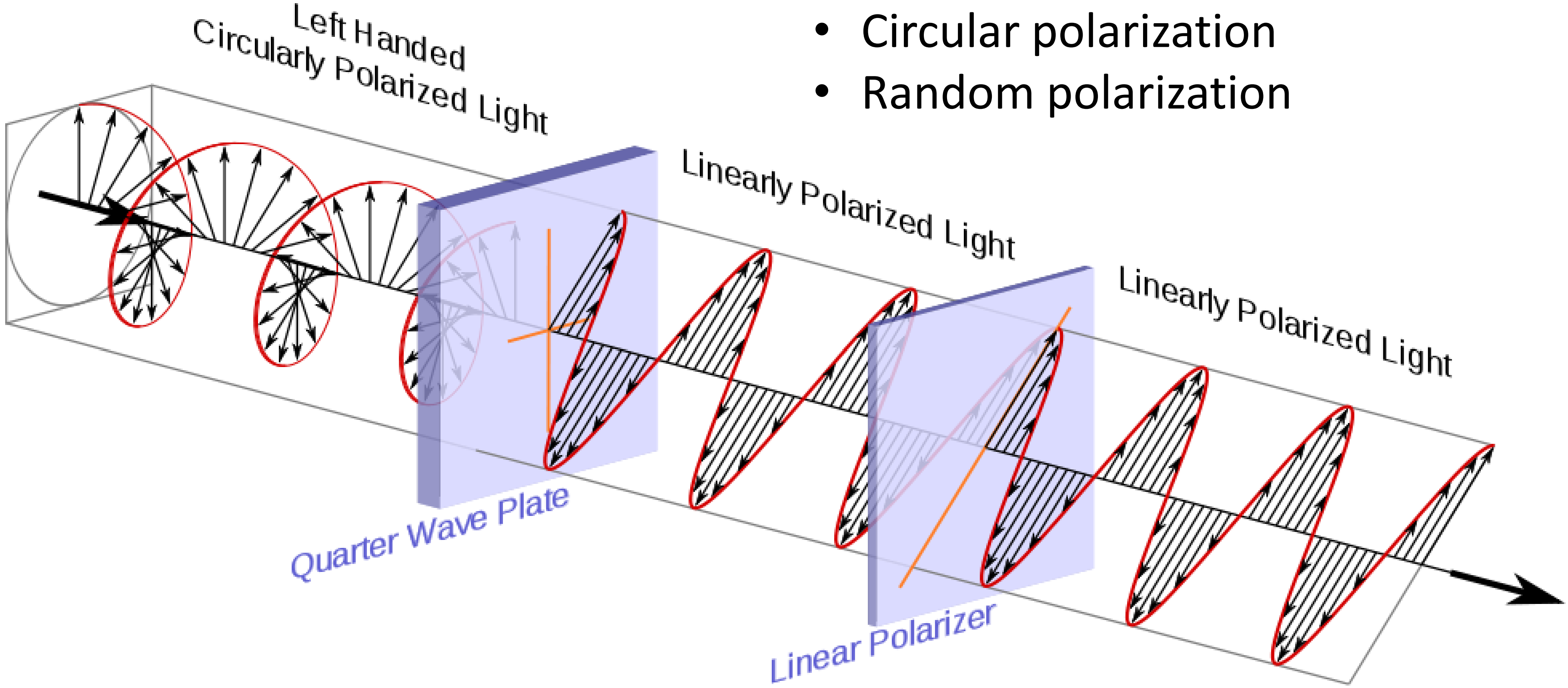


D.I.Y. Graphene: How to Make One-Atom-Thick Carbon Layers With Sticky Tape
Scientific American

Polarization

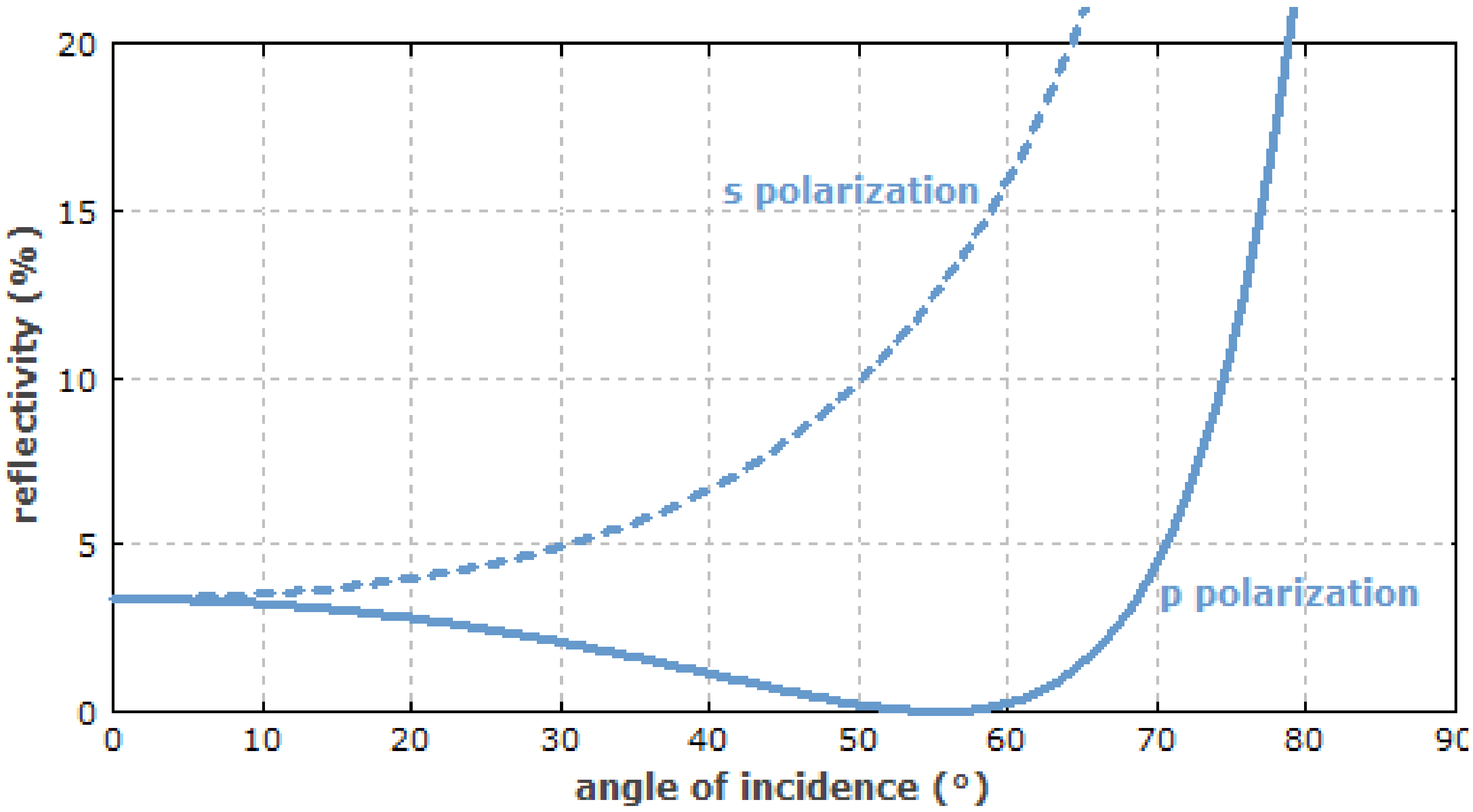
Direction of the electric field in the electromagnetic wave
Mathematically akin to spin (think Bloch sphere)
Simple examples

- Linear polarization
- Circular polarization
- Random polarization



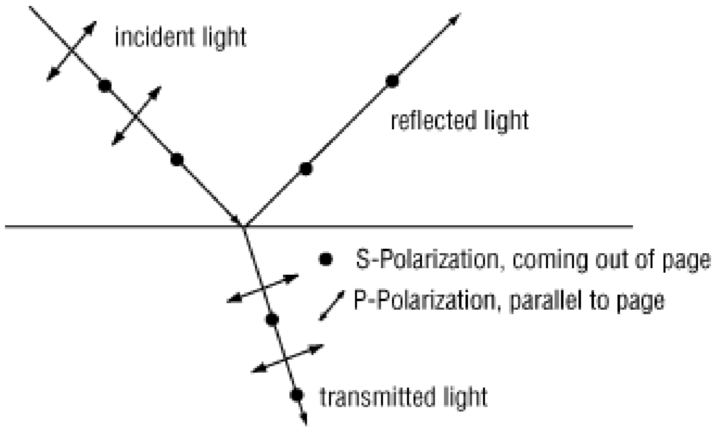
https://en.wikipedia.org/wiki/Polarized_3D_system

Reflectivity Versus Angle of Incidence: Insulator



$R_{norm}=[(n-1)/(n+1)]^2$

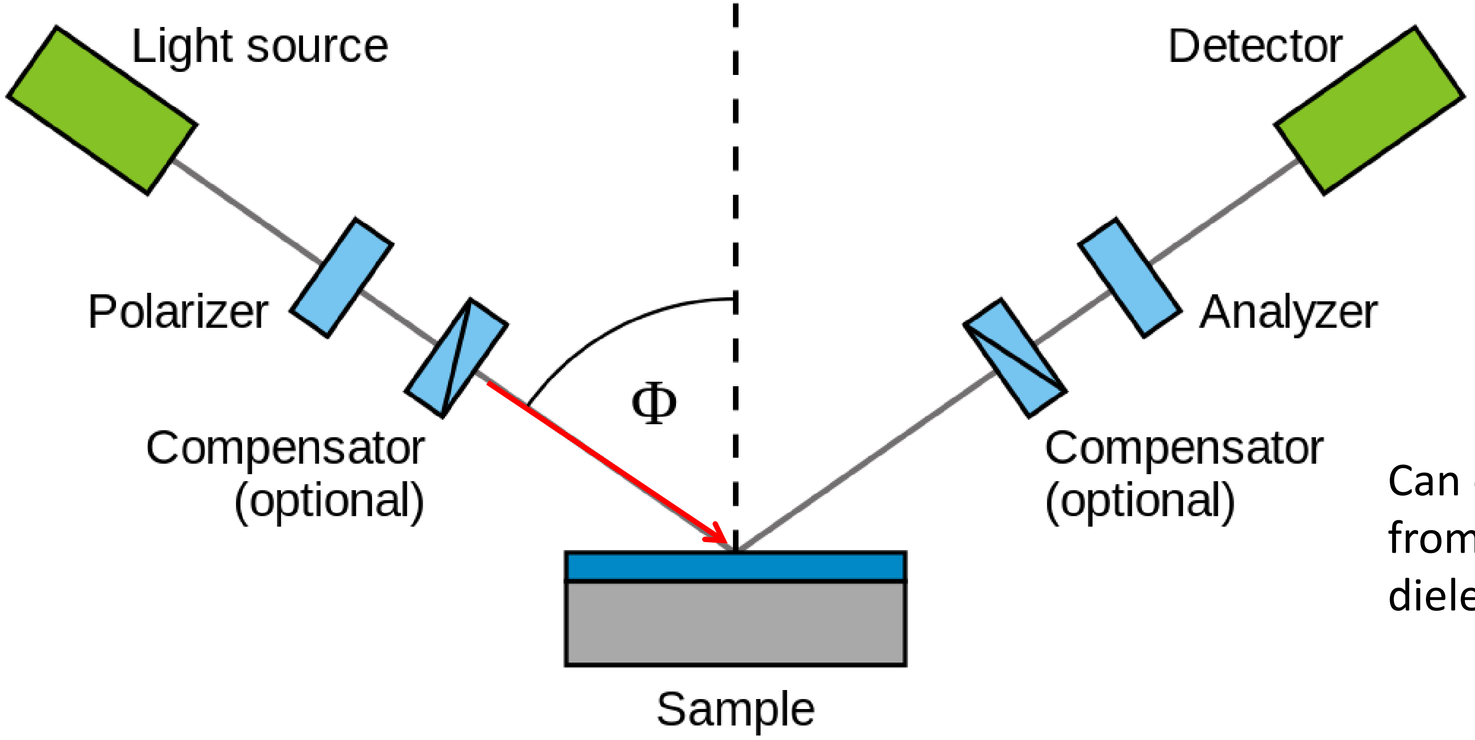
S and P Polarization



Reflectivity is wavelength dependent
Fused Silica RP Photonics Encyclopedia

Edmundoptics.com

Ellipsometry



Can determine complex dielectric constant from thickness OR thickness from complex dielectric constant

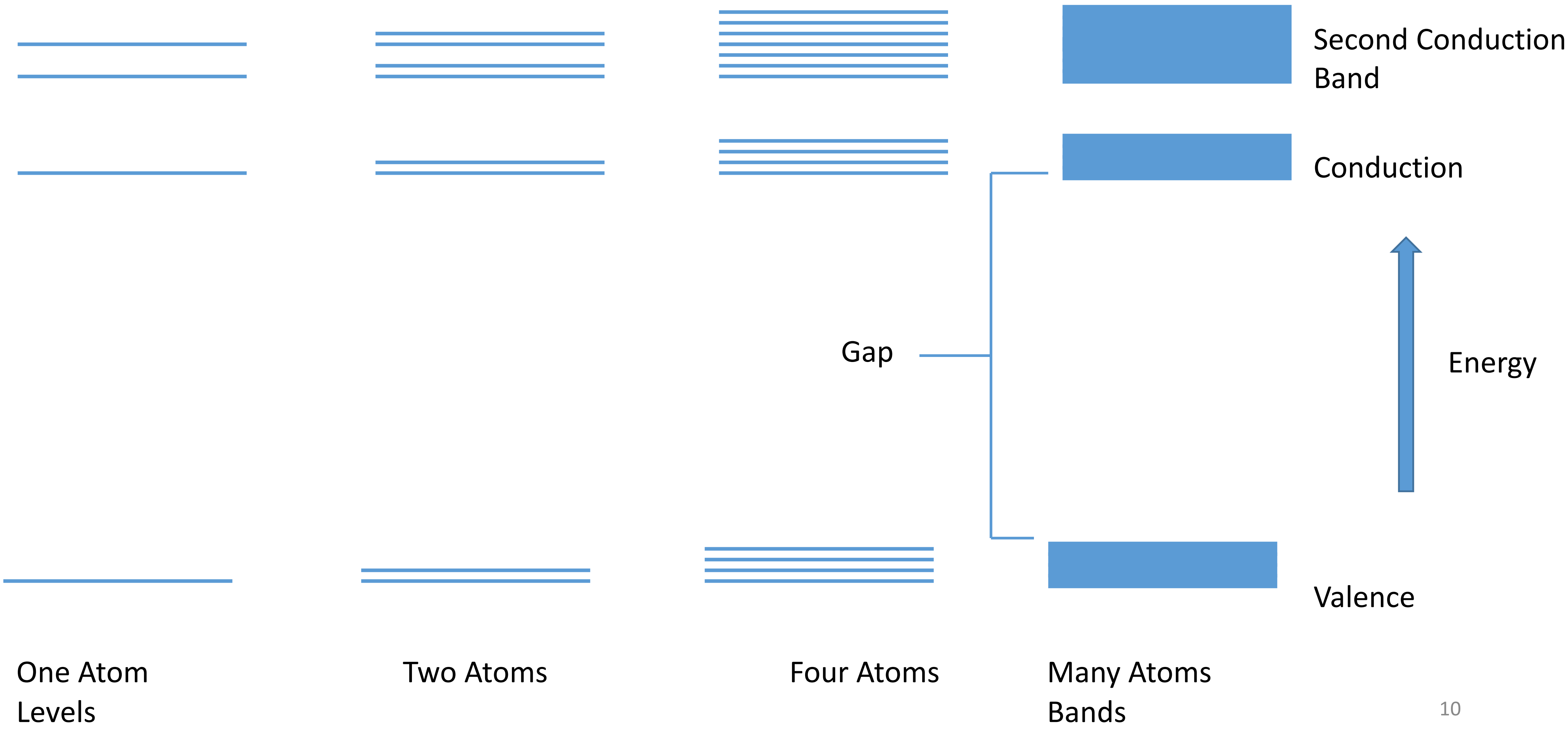
https://en.wikipedia.org/wiki/Ellipsometry

Why is reflectivity important?

- Tells us how light couples into a material (p typically absorbed more than s)
- Reveals refractive index $R_{norm}=[(n-1)/(n+1)]^2$ Dielectric Constant
- Reduced by transitions between states
- Transmission

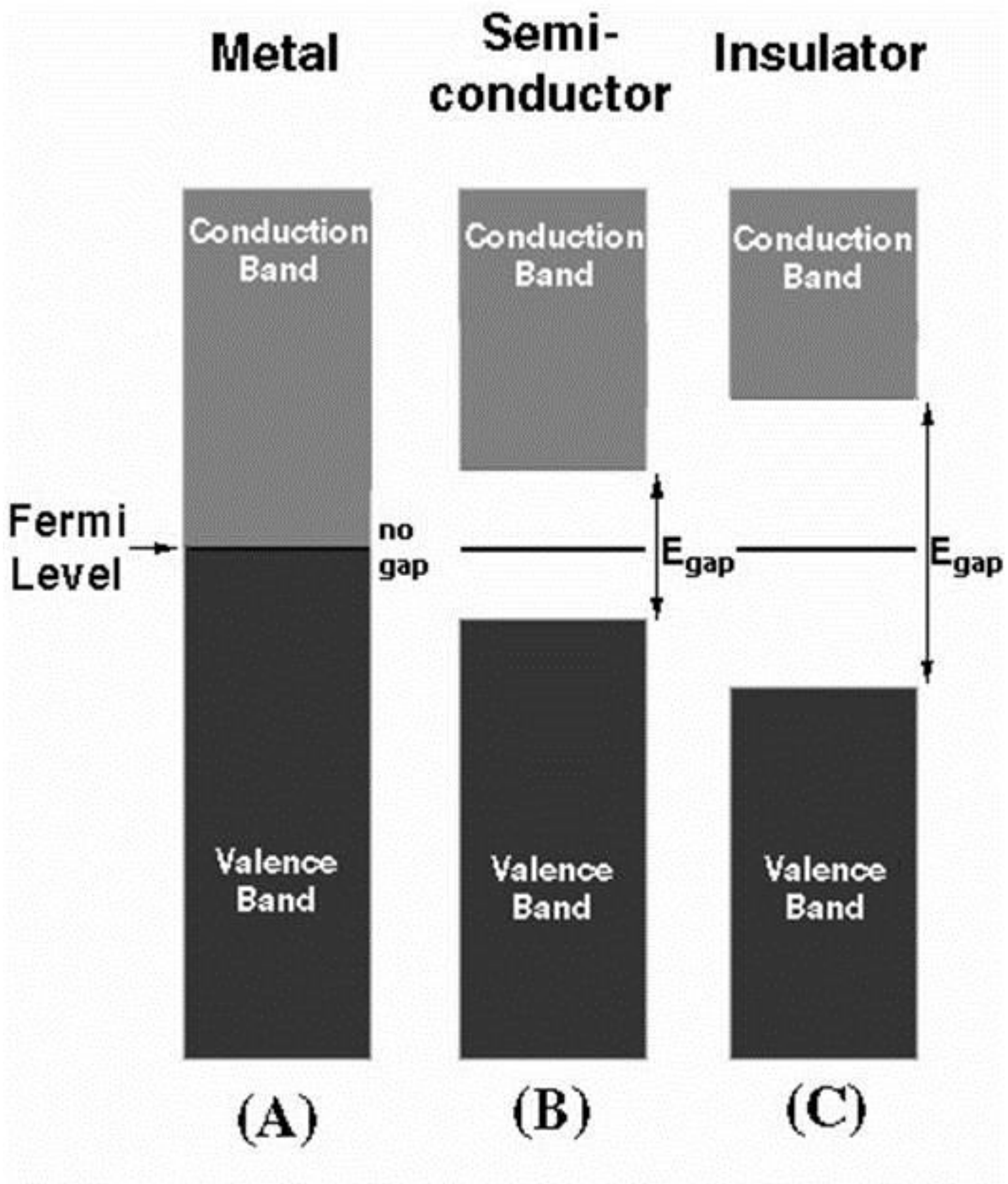
Bands

Atomic interactions shift energy levels when there are several atoms



Bands: Three Kinds of Electronic Materials

Bandgap determines conductivity and optical spectrum



Definitions

- Conductor: Fermi level is *in a band*
- Semiconductor: Fermi level is *in the gap* between bands
- Bandgap: range with no states between bands in a semiconductor
  - Bandgap adjusts conductivity
  - Conductivity is complicated
- HOMO=Valence
  - HOMO=Highest Occupied Molecular Orbital
- LUMO=Conduction
  - LUMO=Lowest Unoccupied Molecular Orbital

Usually we talk about conduction and valence because other bands are hard to access

Monolayers have fewer states in each band

Laszlo’s Speculation: Higher and lower lying bands are easier to study and more important in monolayers

Conservation Laws and Dispersion

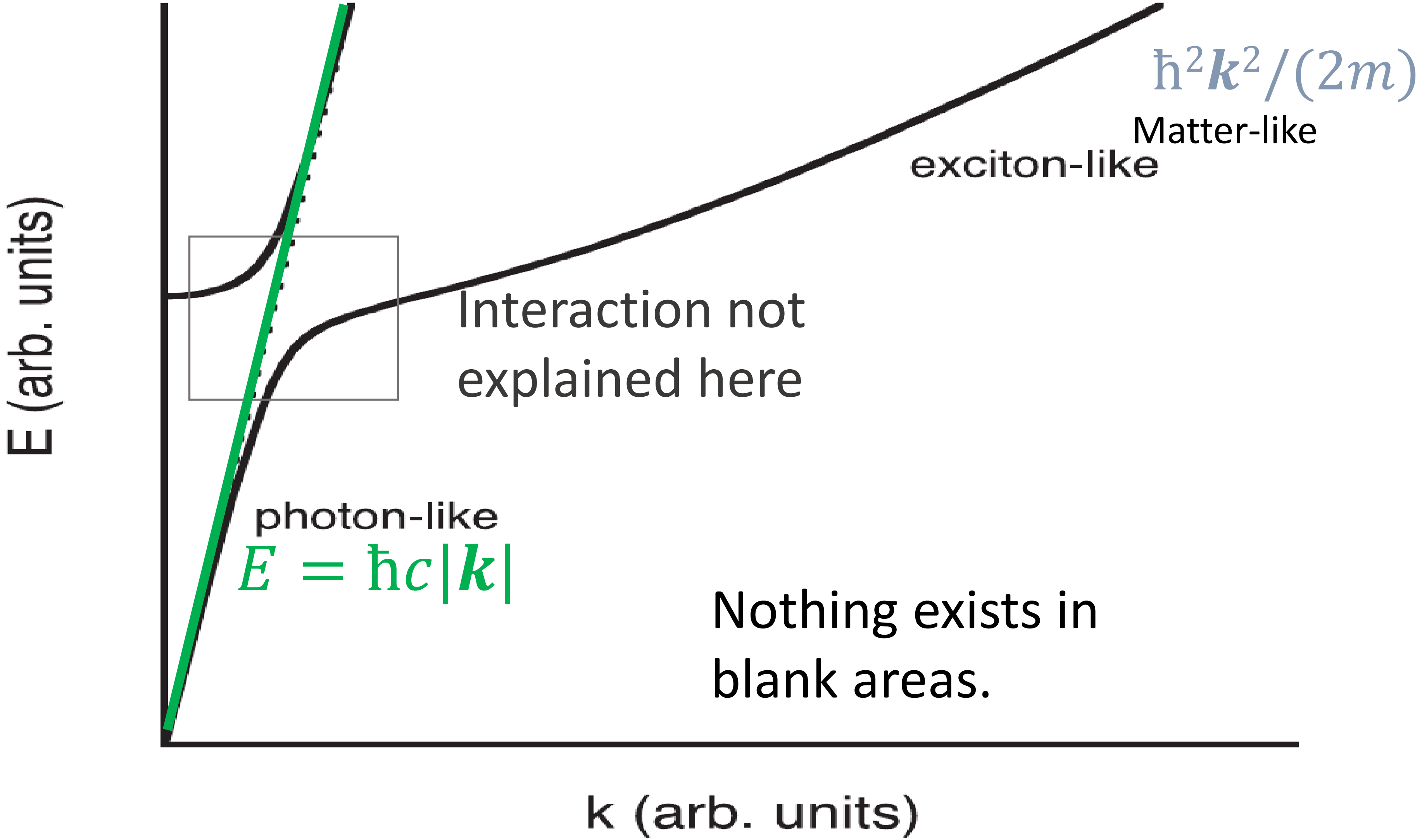
- Conservation of energy: Total energy does not change with time
  - $E_{in} = E_{out}$

- Conservation of momentum: Total momentum does not change with time
  - $\mathbf{k}_{in} = \mathbf{k}_{out}$

- Dispersion: Energy/momentum relationship for particles
  - Free electron $E = \hbar^2 \boldsymbol{k}^2/(2m)$

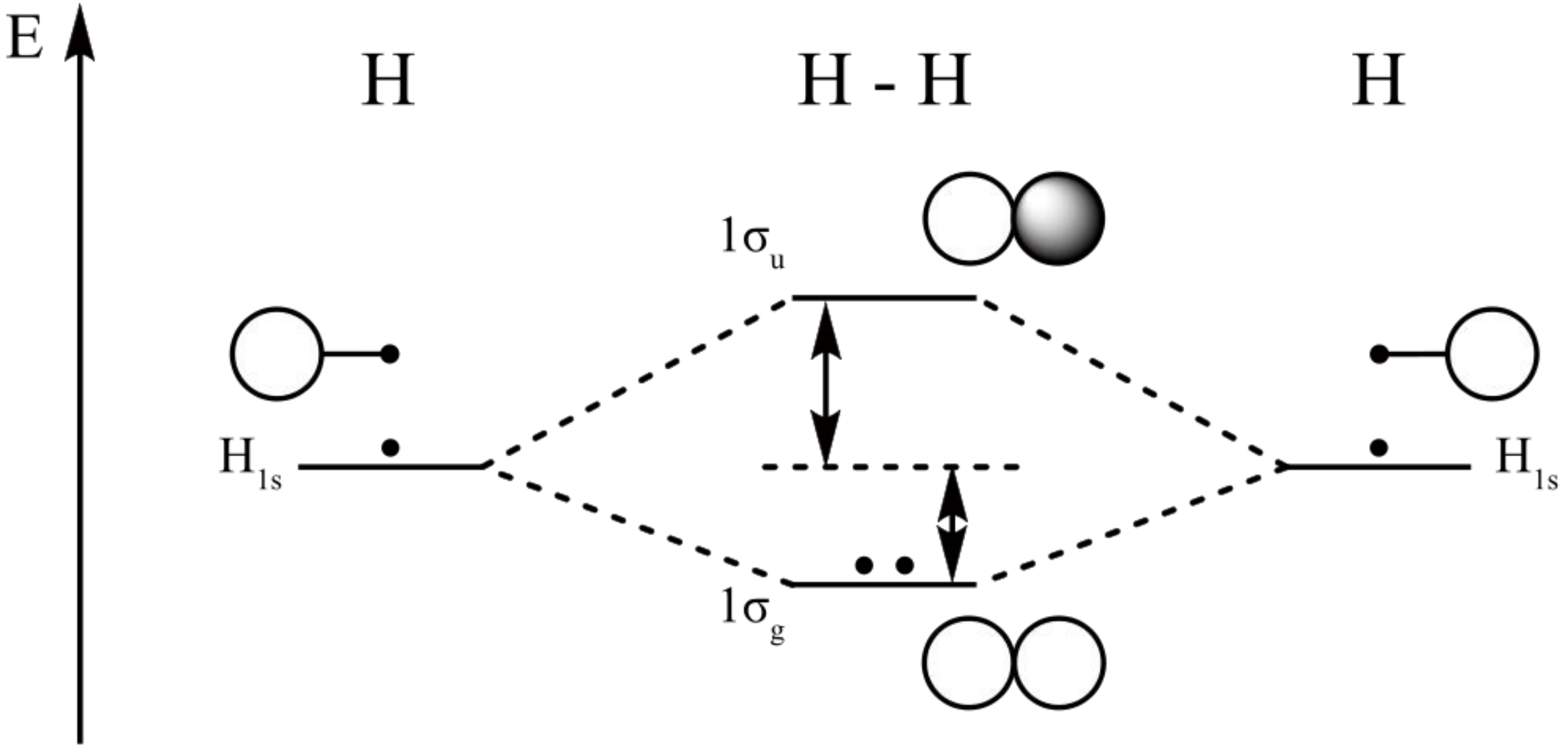
Dispersion: Energy/Momentum Relationship

When two dispersions cross, interactions obey energy and momentum conservation

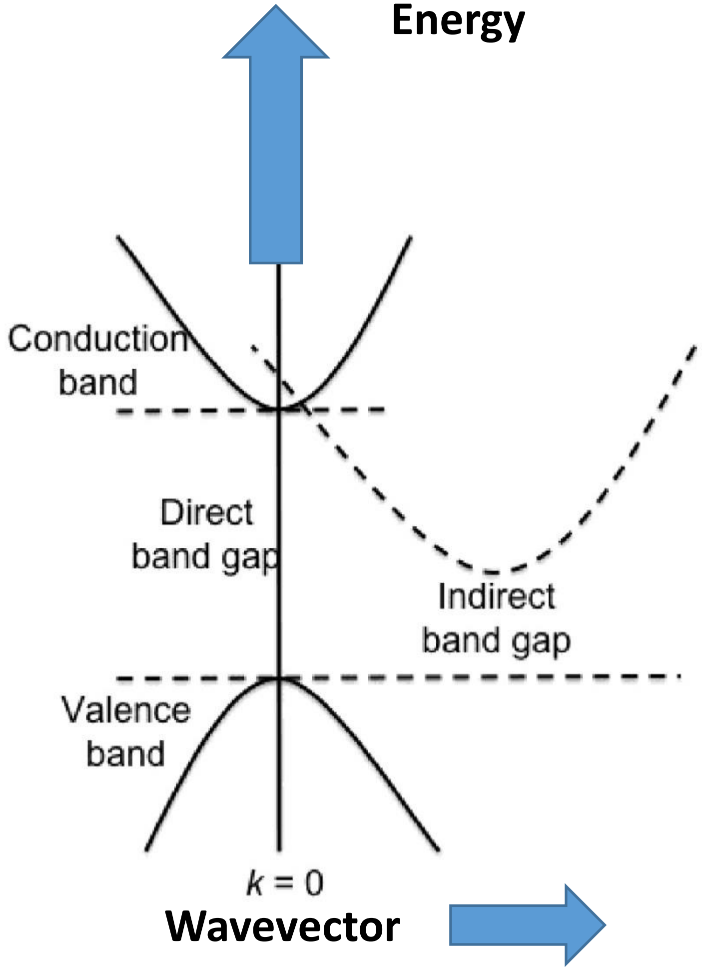


Snoke, David. "Spontaneous Bose coherence of excitons and polaritons." Science 298.5597 (2002): 1368-1372.

Band Diagrams vs. Molecular Potential Energy Surfaces

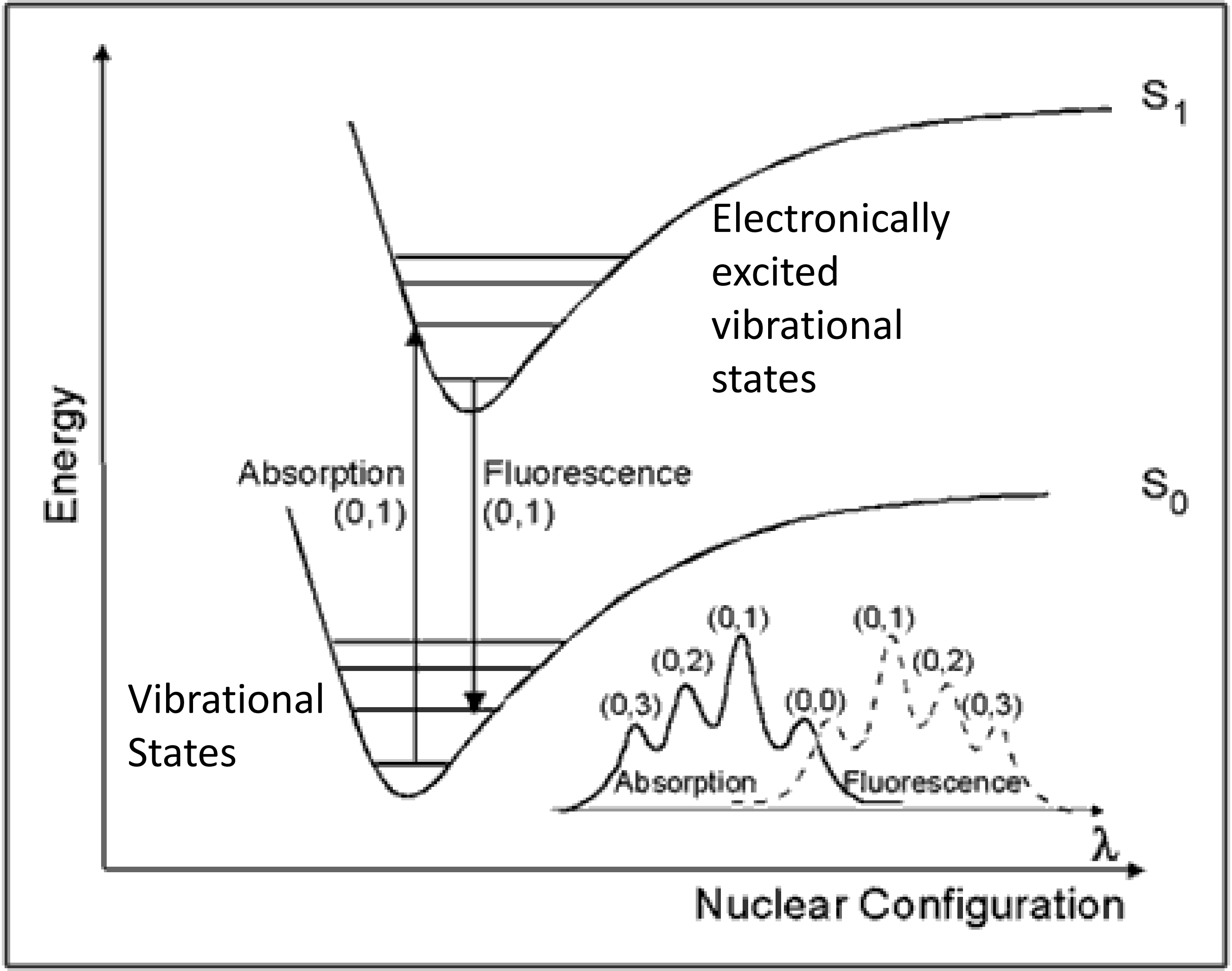


https://en.wikipedia.org/wiki/Molecular_orbital_diagram

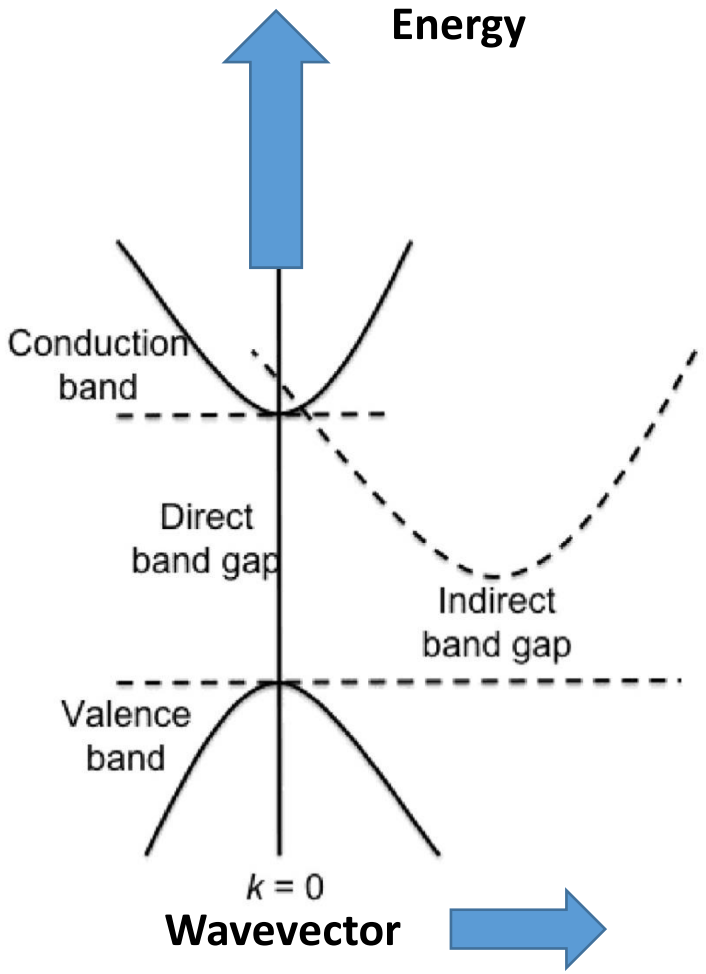


http://solarwiki.ucdavis.edu/The_Science_of_Solar/Solar_Basics/C._Semiconductors_and_Solar_Interactions/III._Absorption_of_Light_and_Generation/2._Direct_Semiconductors?sa=X&ved=0CBoQ9QEwAmoVChMIg5u7r5P-xgIViVw-Ch1Ozgqy

Band Diagrams vs. Molecular Potential Energy Surfaces



http://www.photobiology.info/Photochem.html



http://solarwiki.ucdavis.edu/The_Science_of_Solar/Solar_Basics/C._Semiconductors_and_Solar_Interactions/III._Absorption_of_Light_and_Generation/2._Direct_Semiconductors?sa=X&ved=0CBoQ9QEwAmoVChMIg5u7r5P-xgIViVw-Ch1Ozgqy

Similarities and Differences: Molecule/Crystal

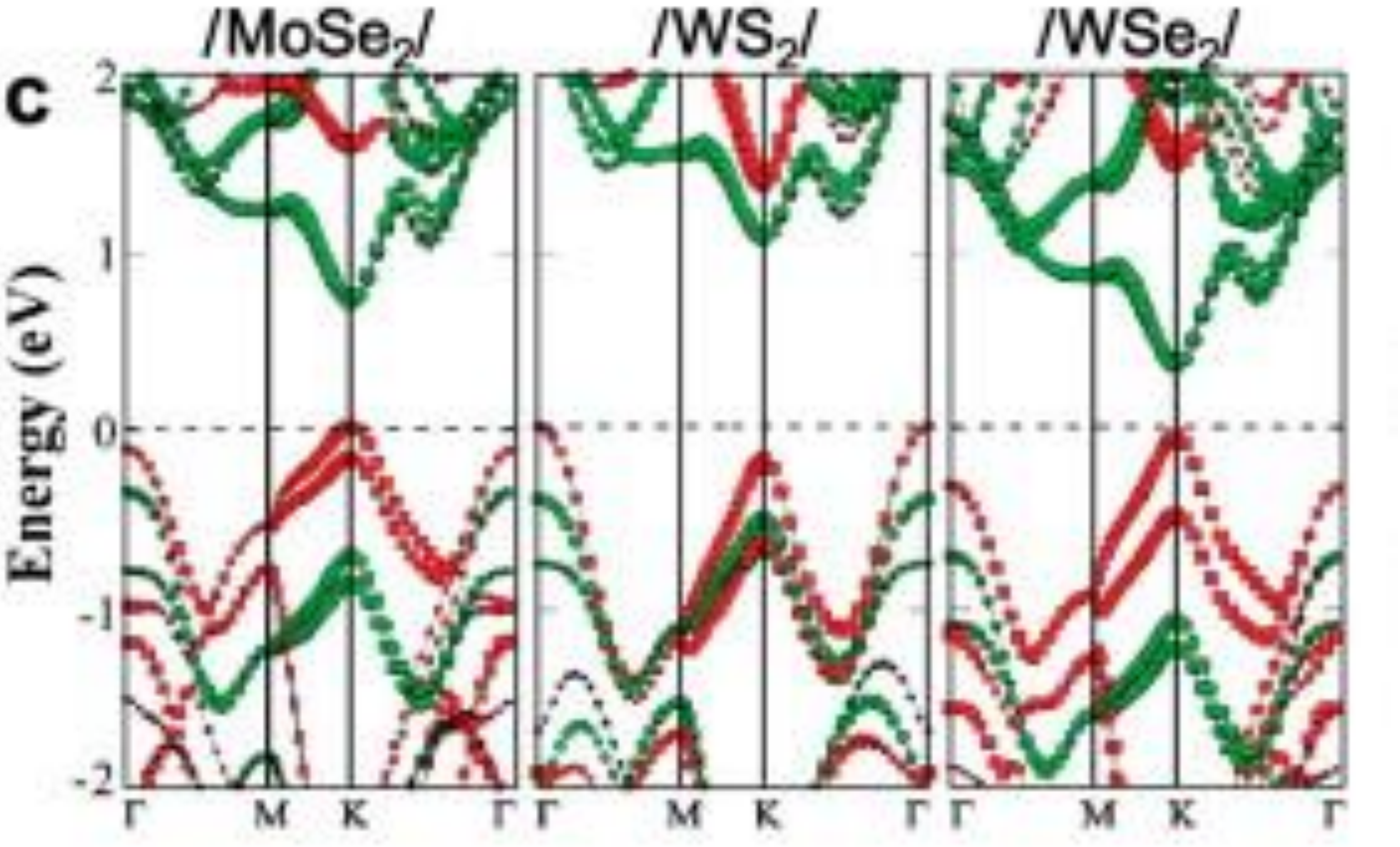
- Similarities
  - Emission at longer wavelength than absorption
  - Energy gaps
  - Absorption can excite electronically and vibrationally
- Differences
  - More electrons in a crystal
  - Momentum in crystal instead of position in molecule

Band Diagrams

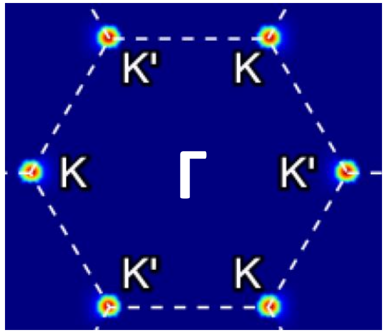
Three parts of band diagrams

1. Energy
2. Wavevector
3. Reciprocal Lattice (X, M, R…)

Energy level can depend on momentum. A band diagram is like an energy level diagram which shows momentum dependence.



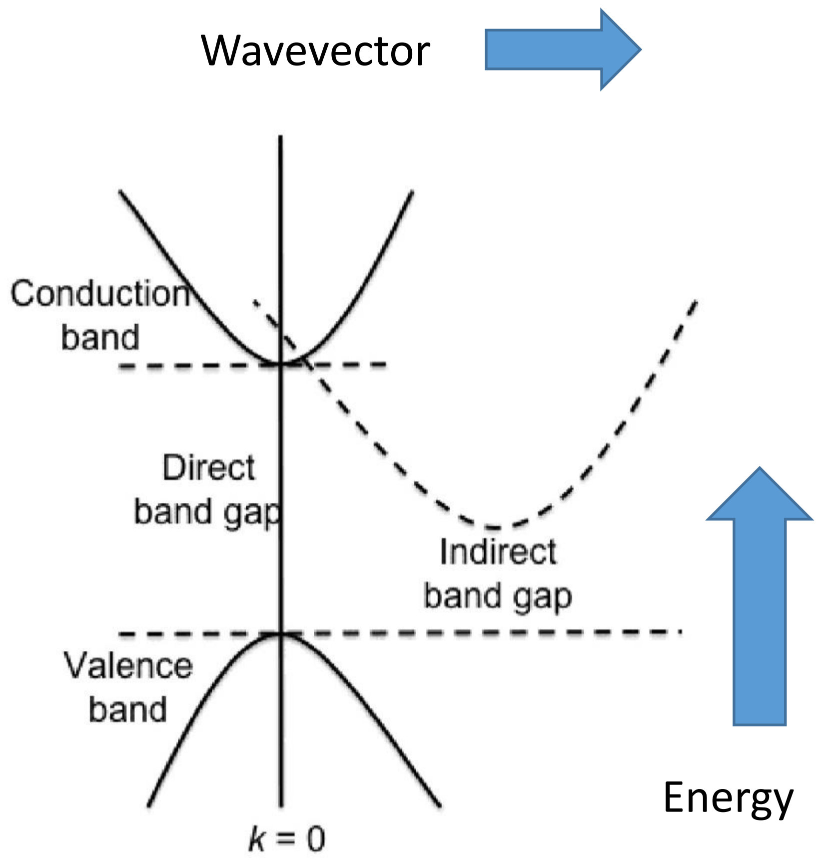
Wavevector and Reciprocal Lattice



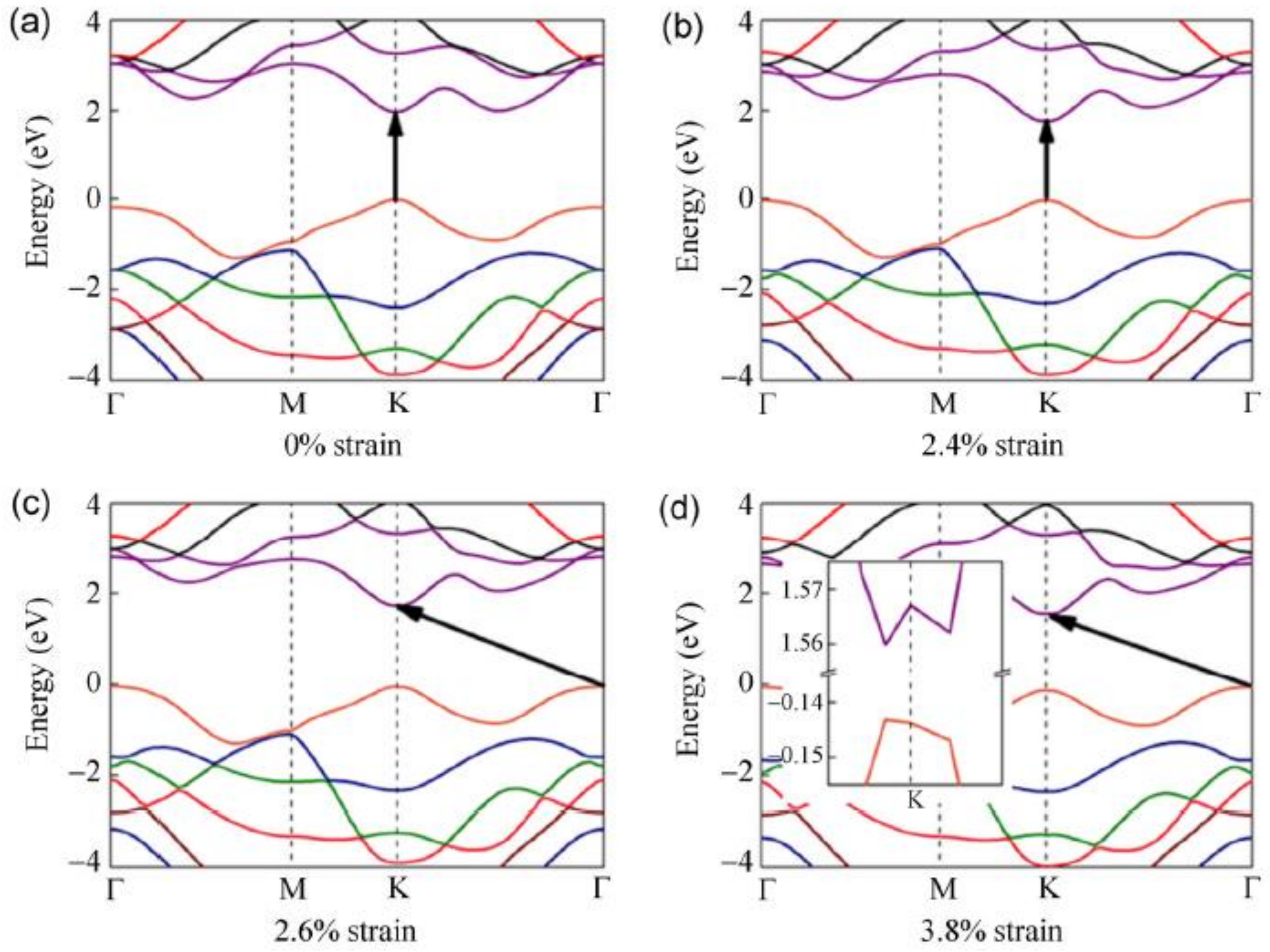
Tianchao Niu, Ang Li, *From two-dimensional materials to heterostructures,* Surf. Sci. (2015), **90** (1), 25-41,

Direct and Indirect Gap

WS$_2$

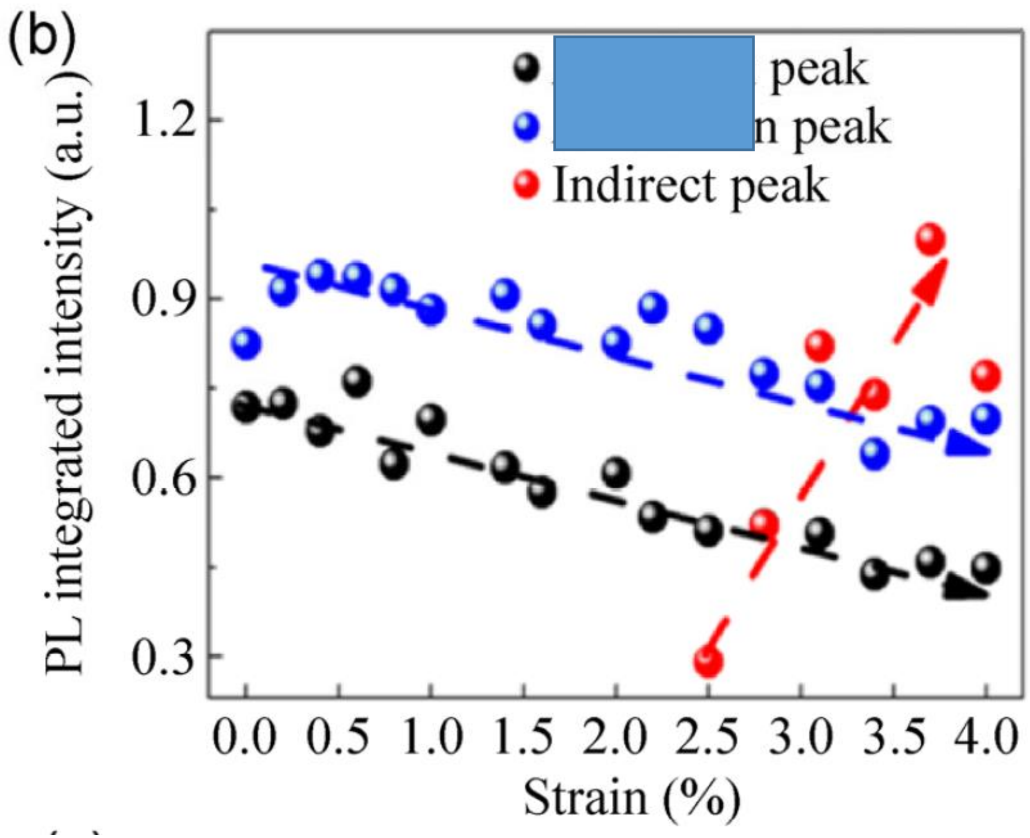


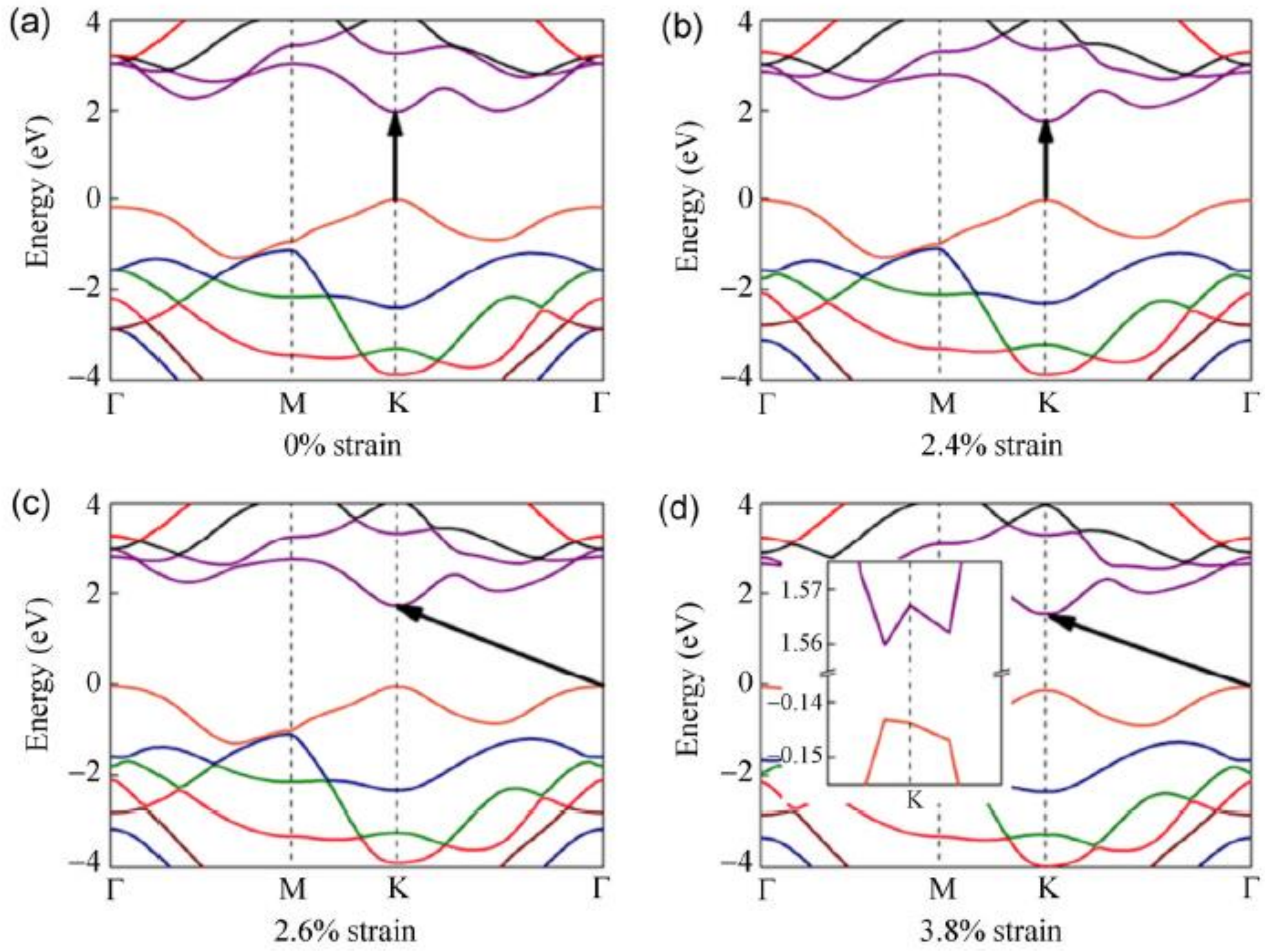
http://solarwiki.ucdavis.edu/The_Science_of_Solar/Solar_Basics/C._Semiconductors_and_Solar_Interactions/III



Wang, Yanlong, Chunxiao Cong, Weihuang Yang, Jingzhi Shang, Namphung Peimyoo, Yu Chen, Junyong Kang, Jianpu Wang, Wei Huang, and Ting Yu. "Strain-induced direct–indirect bandgap transition and phonon modulation in monolayer WS2." Nano Research (2015): 1-11.

Direct and Indirect Gap: Absorption and Luminescence





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Quasiparticles

- Quantum of Energy in a Crystal
- Multiple classes of quasiparticles
- Emergent property of large numbers of atoms

Quasiparticles Important to Optics

- Electron – In my opinion it counts as "quasi" when it is interacting with its surroundings. Quasiparticle electron mass can be different from free electron mass.
- Hole (antielectron)
- Exciton (electron+hole) + sign means particles bound by an attractive force
- Biexciton (exciton+exciton)
- Trion (exciton+electron OR exciton+hole)
- Exciton Polariton (electron+hole+photon)
- Phonon (sound)

Some quasiparticles appear in nature, others only appear in man-made experiments

Exciton States

- H atom potential. $V=-e^2/(4\pi\varepsilon r)$

- Dielectric environment Why does salt dissolve in water?

- Only in direct gap semiconductors where conduction maximum and valence minimum are at same place in reciprocal lattice

- Two types of exciton: Frankel or Wannier-Mott

- Exciton structure analogous to hydrogen atom structure

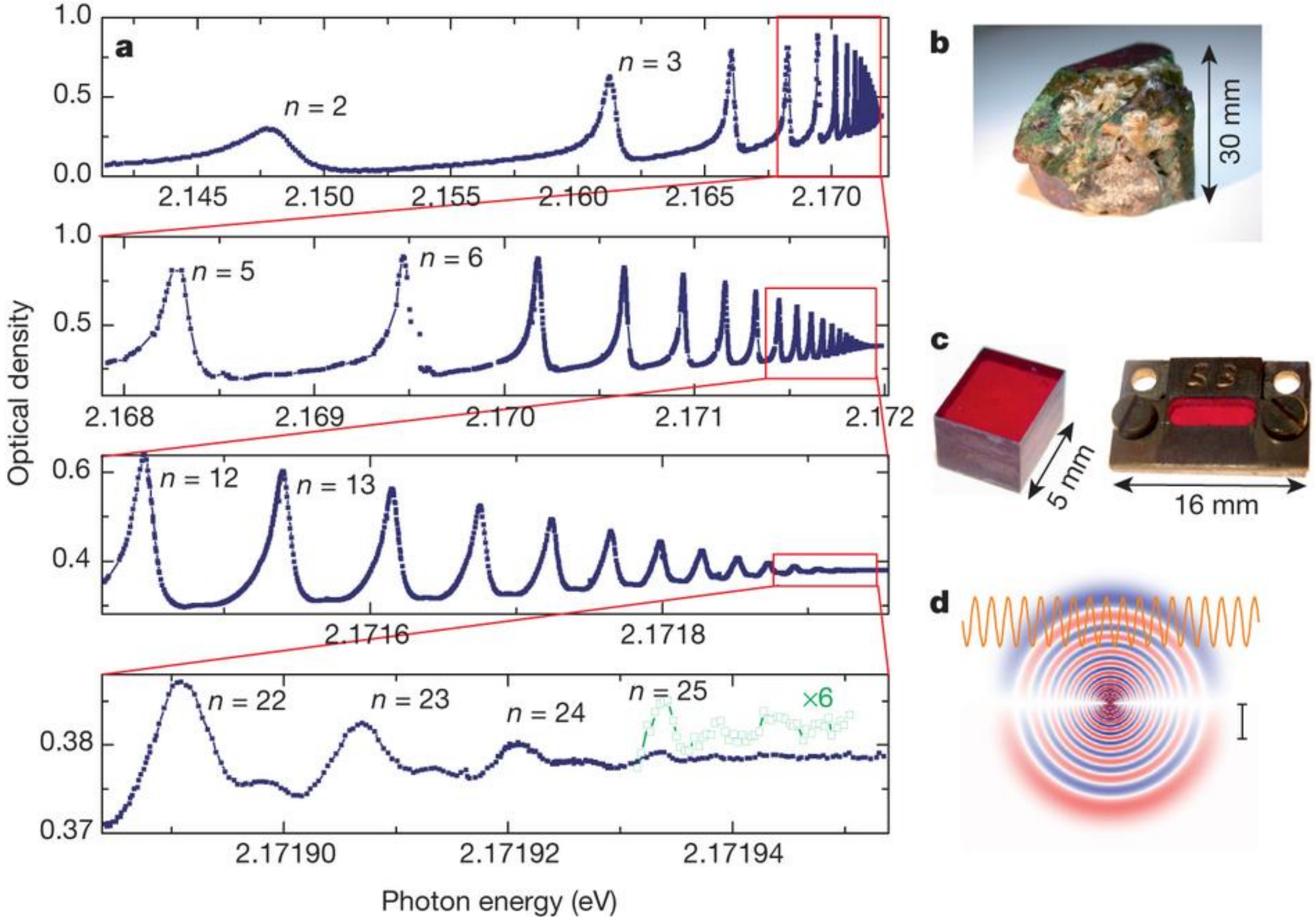
Discovery of Excitons

Predicted 1931 Frenkel
Discovered 1951 E. F. Gross in Cuprous Oxide

$V = -e^2/(4\pi\varepsilon r)$

$E_n \propto 1/n^2$

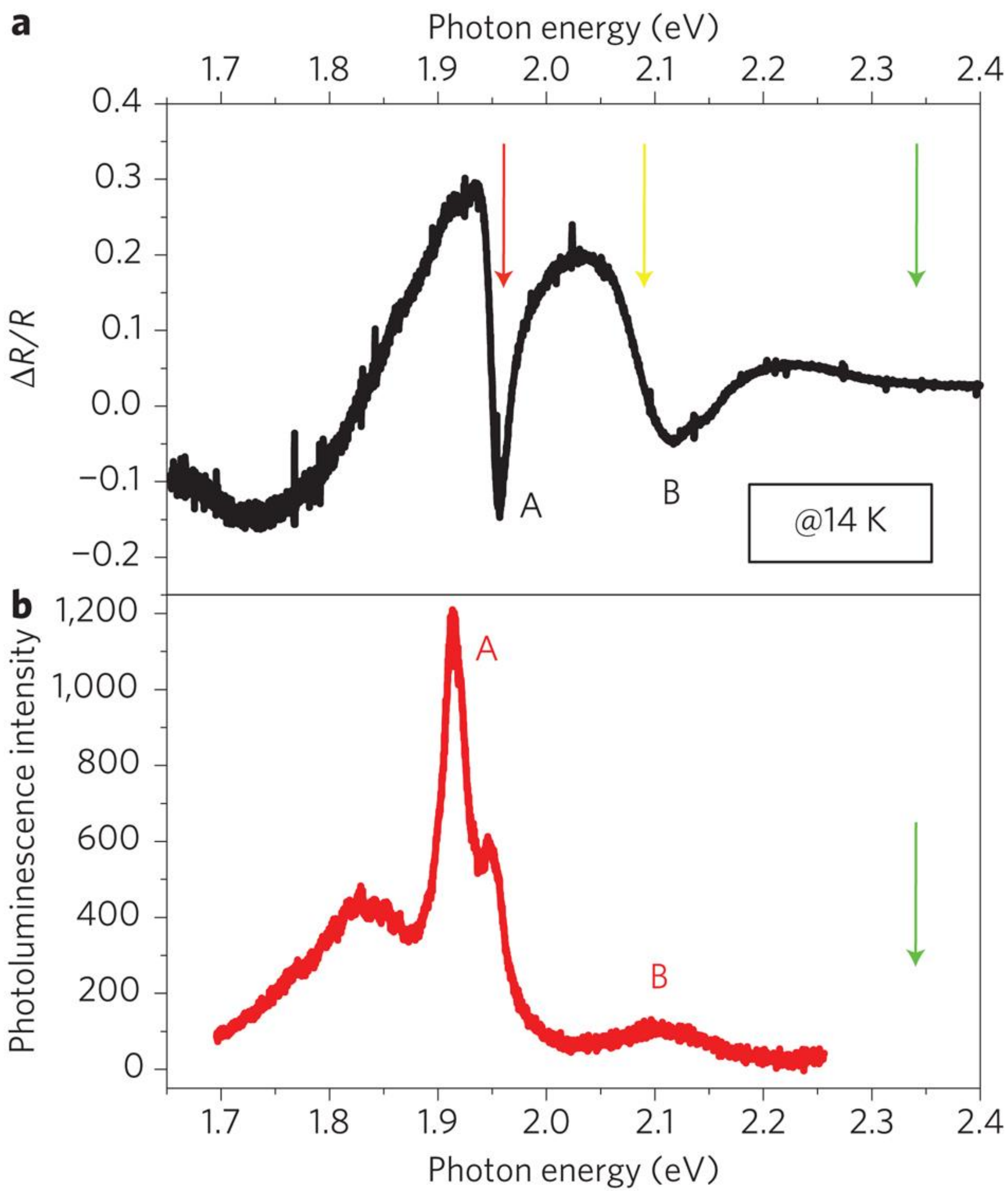
Not generally this simple.



Kazimierczuk, T., D. Fröhlich, S. Scheel, H. Stolz, and M. Bayer. "Giant Rydberg excitons in the copper oxide Cu2O." Nature 514, no. 7522 (2014): 343-347.

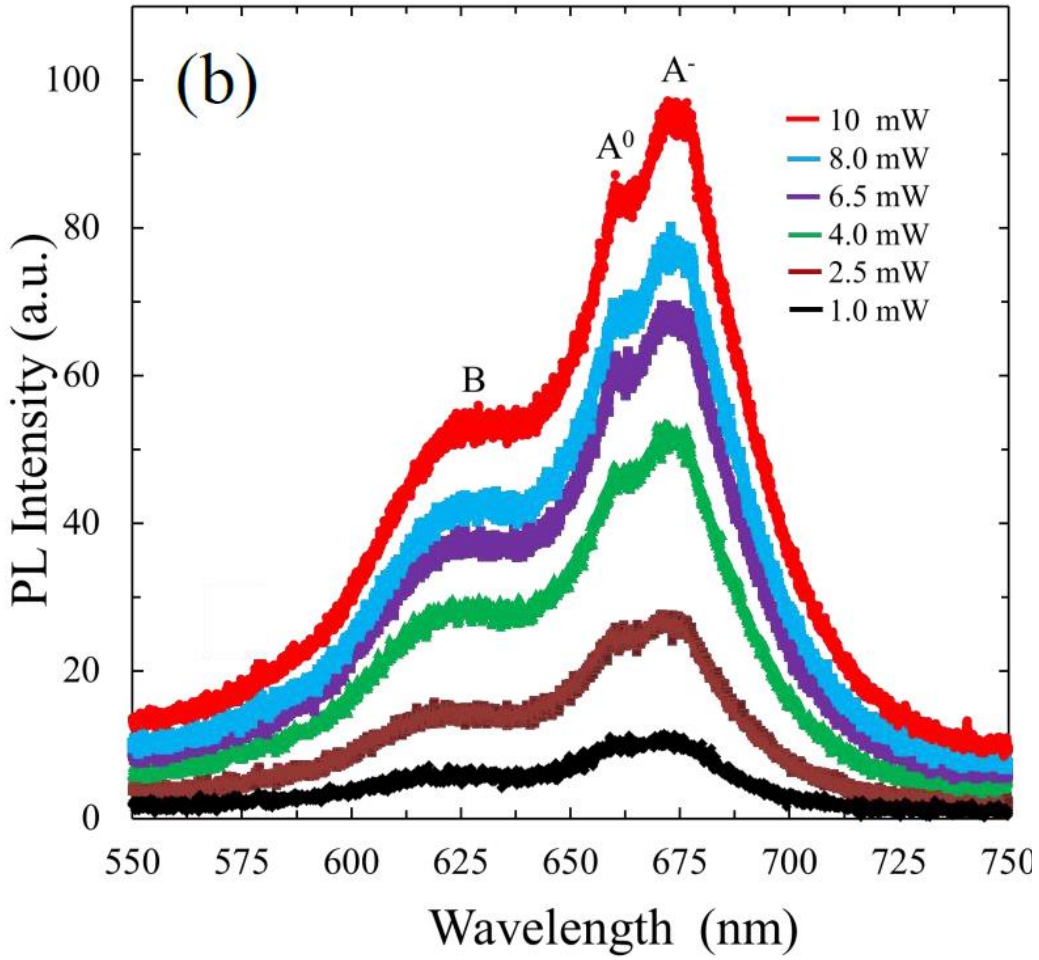
Signature of an Exciton

- Absorption/Luminescence Resonance
- Below Bandgap



Mak, Kin Fai, Keliang He, Jie Shan, and Tony F. Heinz. "Control of valley polarization in monolayer MoS2 by optical helicity." *Nature nanotechnology* 7, no. 8 (2012): 494-498.

Excitons, Trions, and Biexcitons From Luminescence and Transient Absorption

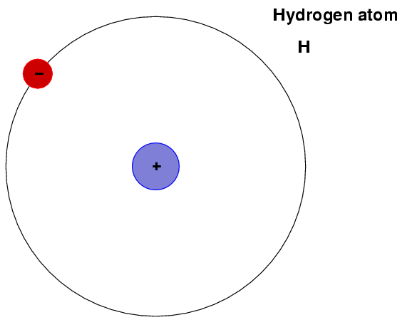


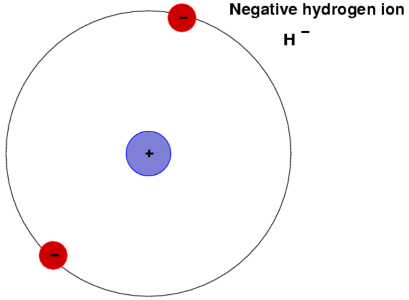
Trion in Molybdenum Disulfide

Taghinejad, Hossein, Mohammad Taghinejad, Alexey Tarasov, Meng-Yen Tsai, Amir H. Hosseinnia, Philip M. Campbell, Ali A. Eftekhar, Eric M. Vogel, and Ali Adibi. "Nonlinear Raman Shift Induced by Exciton-to-Trion Transformation in Suspended Trilayer MoS2." arXiv preprint arXiv:1502.00593 (2015).

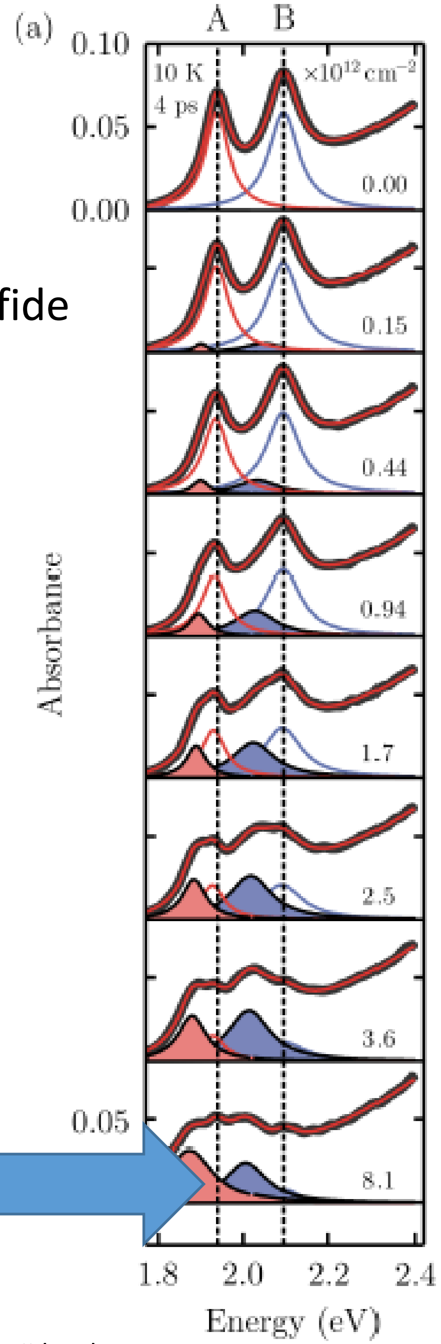
Biexciton on molybdenum disulfide

Sie, Edbert J., Yi-Hsien Lee, Alex J. Frenzel, Jing Kong, and Nuh Gedik. "Biexciton formation in monolayer MoS2 observed by transient absorption spectroscopy." arXiv preprint arXiv:1312.2918 (2013).





http://spiff.rit.edu/richmond/asras/distance_ii/distance_ii.html



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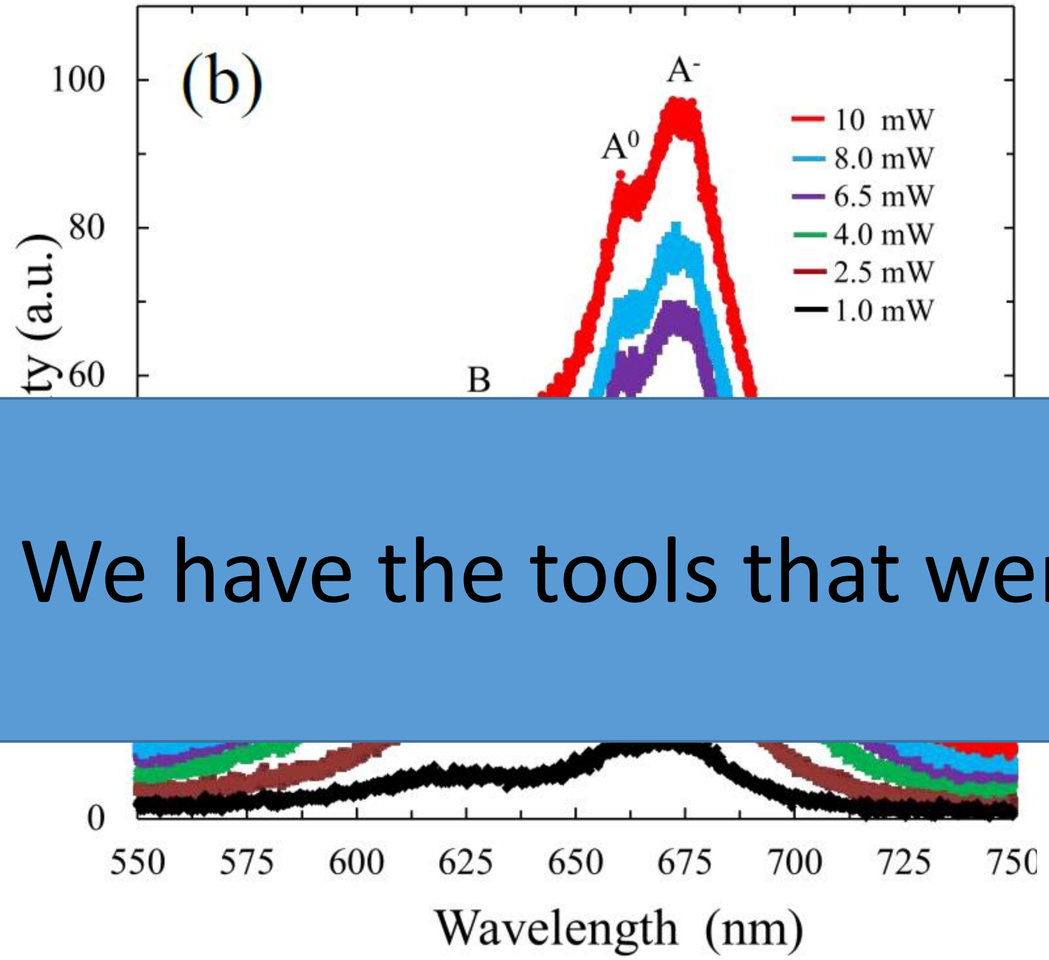
Excitons, Trions, and Biexcitons From Luminescence and Transient Absorption



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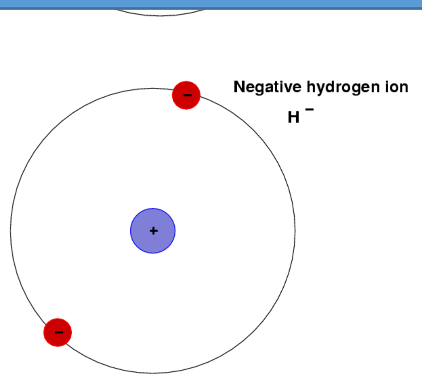

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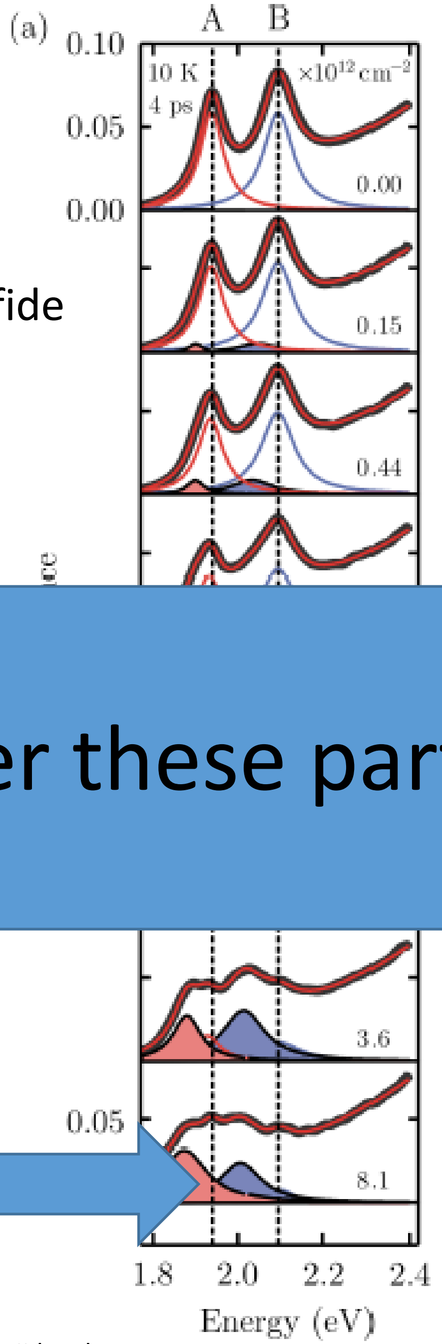

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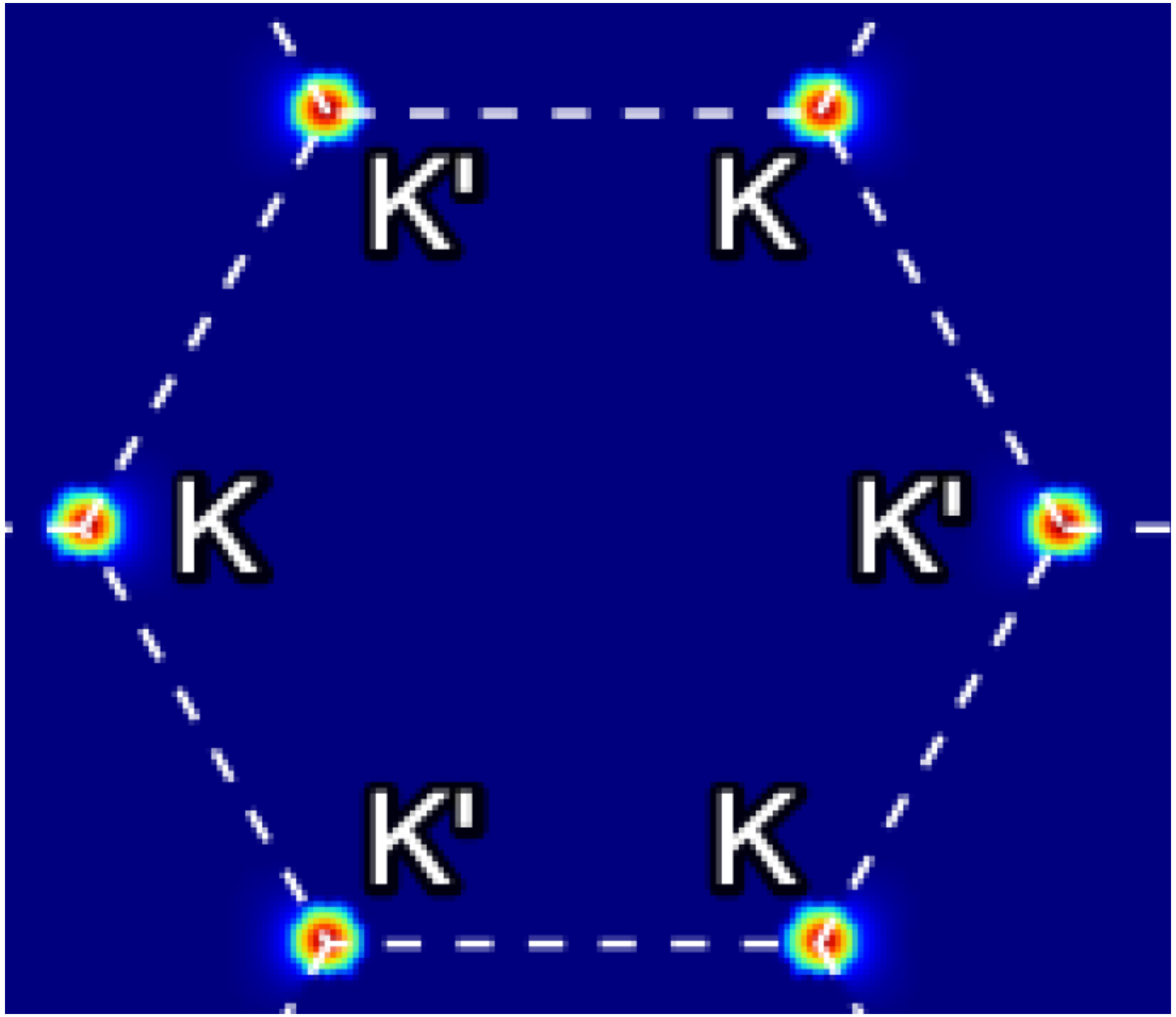
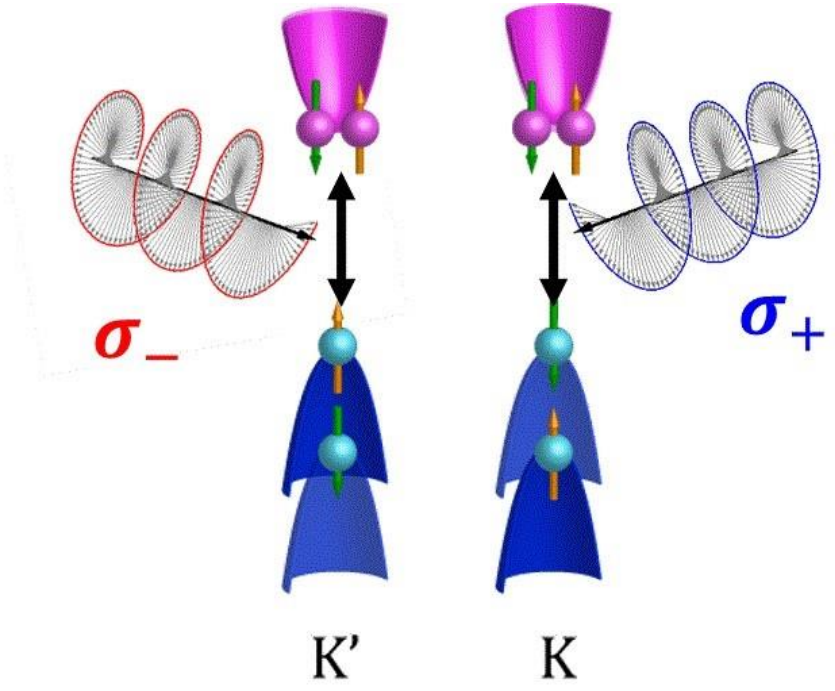
We have the tools that were used to discover these particles.

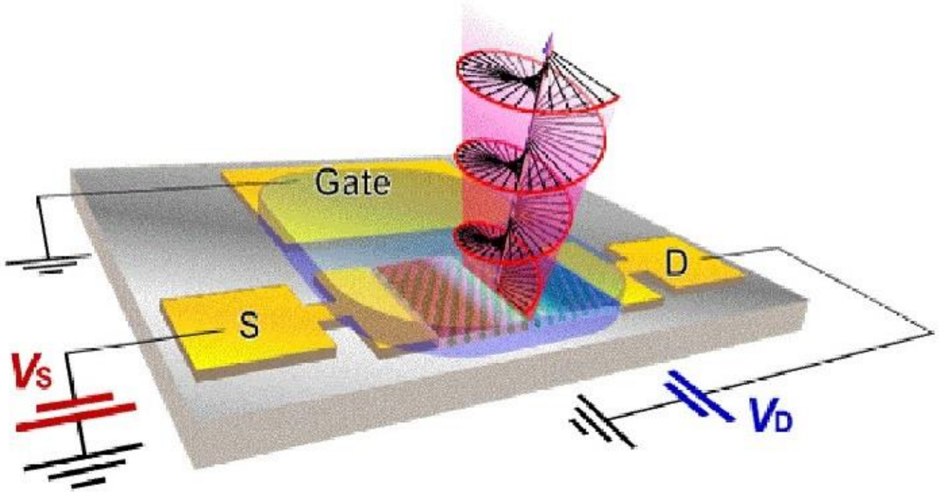
Valley Degree of Freedom

Exction Wavefunction in Reciprocal Space (DFT)

Qiu, D. Y., Felipe, H., & Louie, S. G. (2013). Optical spectrum of MoS 2: many-body effects and diversity of exciton states. Physical review letters, 111(21), 216805.







http://www.qpec.t.u-tokyo.ac.jp/research03-e.html

Valley Decoherence Measurement by Transient Absorption

- Decoherence is a challenge for all quantum computing schemes
- Need ideas for how to reduce intervalley scattering
- **Transient absorption can measure decoherence**

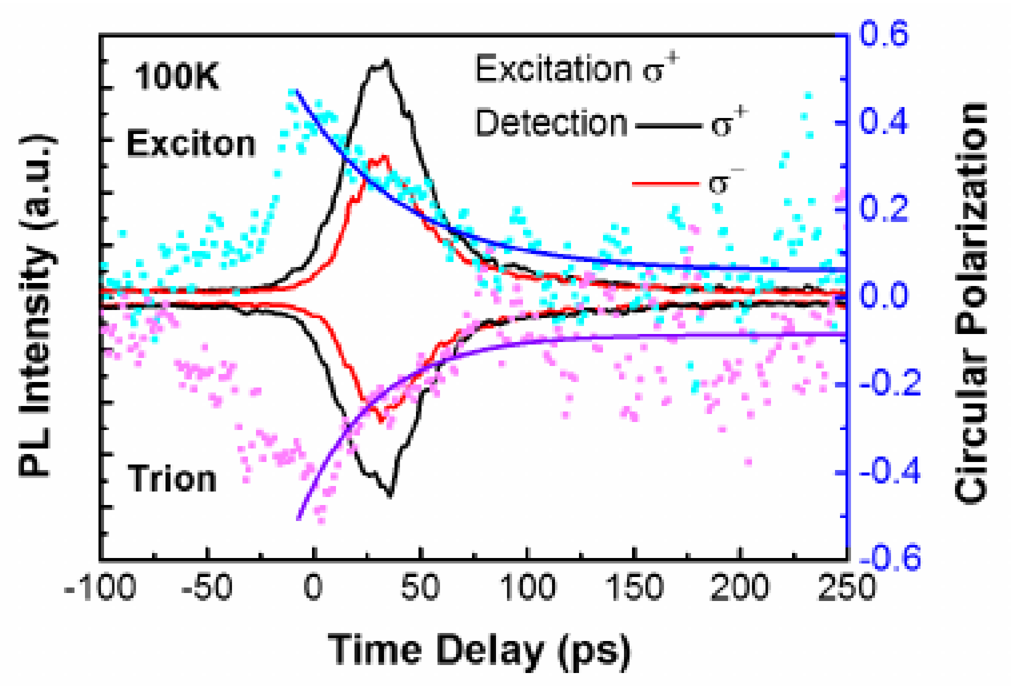


FIG. 2. The time-resolved circularly-polarized PL response of both exciton and trion at 100K with pumping of 1.68eV. The valley polarization lifetime is obtained by fitting the exponential decay function as plotted with blue and violet solid lines.

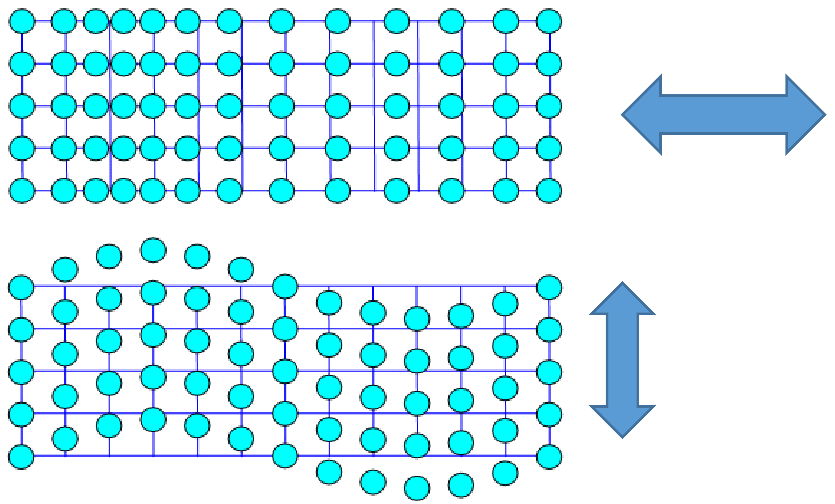
Yan, T., Qiao, X., Tan, P., & Zhang, X. (2015). Valley depolarization in monolayer WSe2. arXiv preprint arXiv:1502.07088.

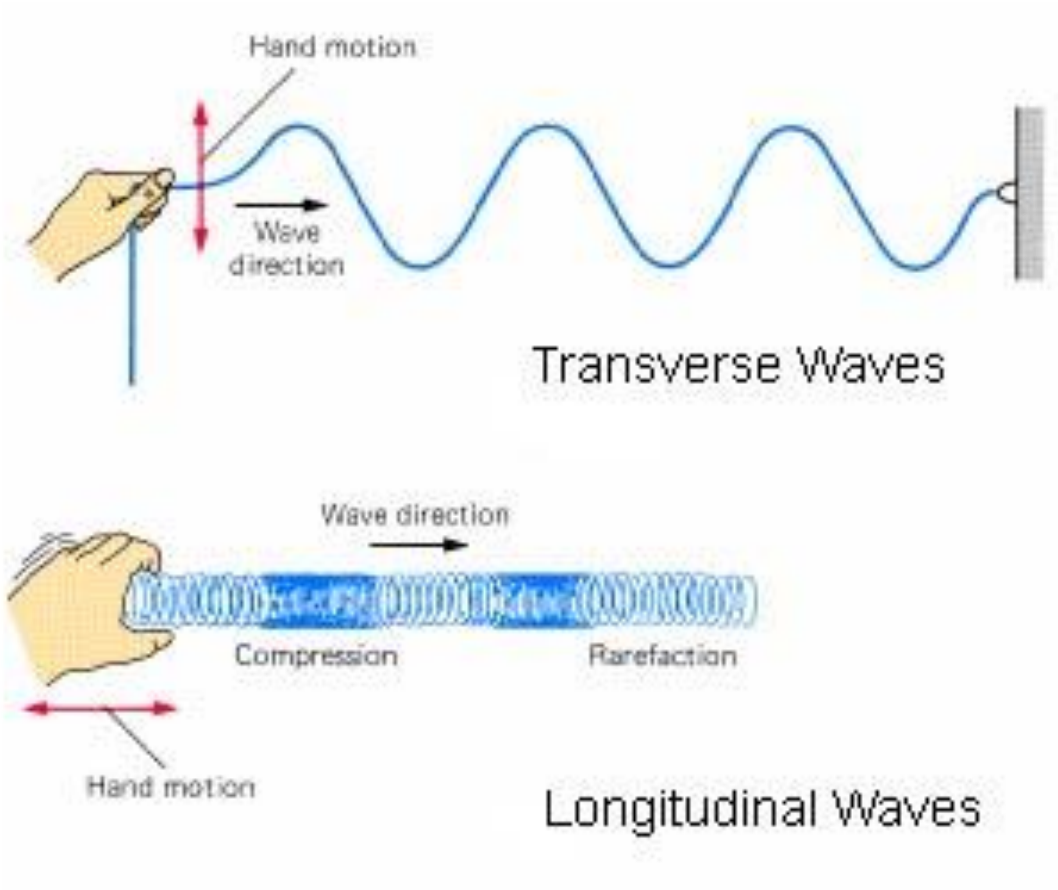
What happens after a photon is absorbed by a solid?

- Metals (no band gap)
    1. Coherent (plasmon) -> dephasing
    2. Hot electron creation
    3. Electron cooling
        1. e-e scattering
        2. e-phonon scattering
- Semiconductor
    1. Hot electron creation
    2. Electron cooling
        1. e-e scattering
        2. e-phonon scattering
    3. e-h pair formation (exciton formation)
    4. e-h pair recombination/light emission

Longitudinal and Transverse Phonons

- Transverse: atomic motion perpendicular to wavevector
- Longitudinal: atomic motion parallel to wavevector
- A video of transverse/longitudinal behavior can help
- Velocity depends on phonon type





http://images.tutorvista.com/cms/images/39/longitudinal-transverse-waves1.jpg
http://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/i4_1_1.html

Phonon Types and Density of States

- Phonons have low energy and huge mass
- Huge mass because nuclei participate by moving
- **Acoustic** phonon bands reach zero energy
  - “Regular” sound
  - Atoms move in phase
- **Optical** phonon bands do not reach zero
  - Atoms of different types are not in phase
- If there is more than one type of atom, the lighter atoms have higher energy phonon bands
- Experiments to measure energy/wavevector:
  - Raman scattering near Γ point in phonon dispersion because light has low momentum

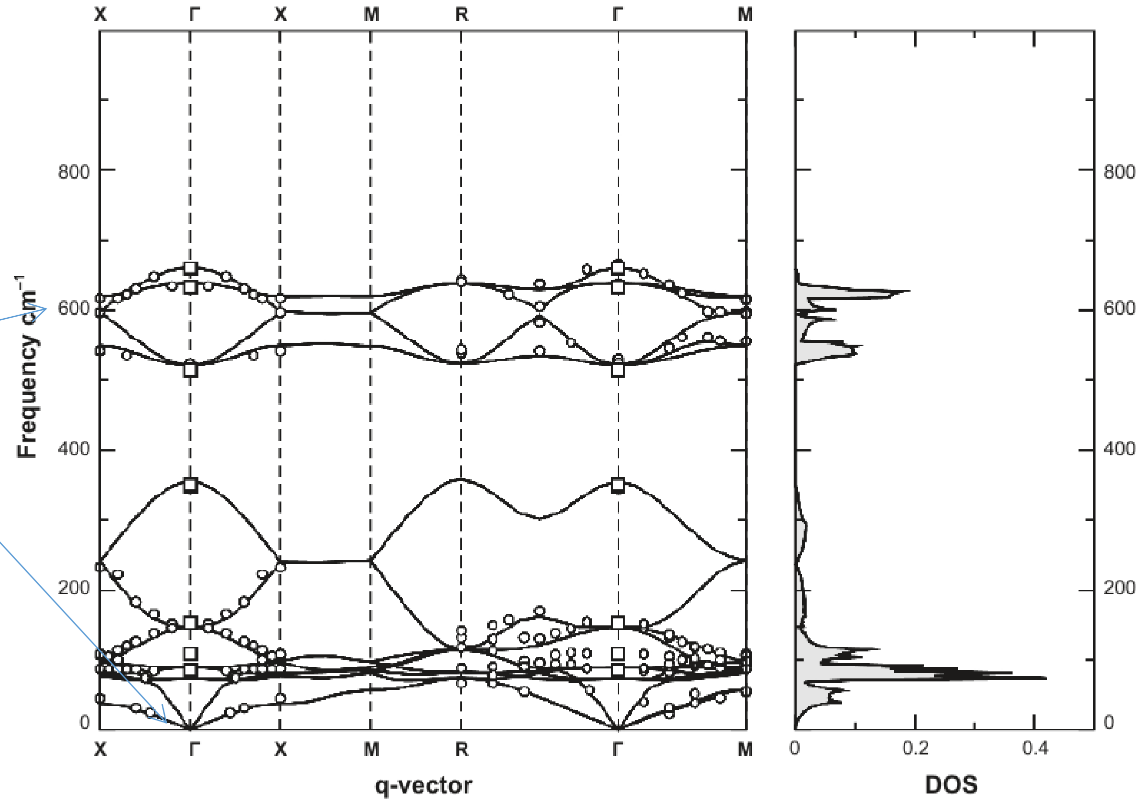
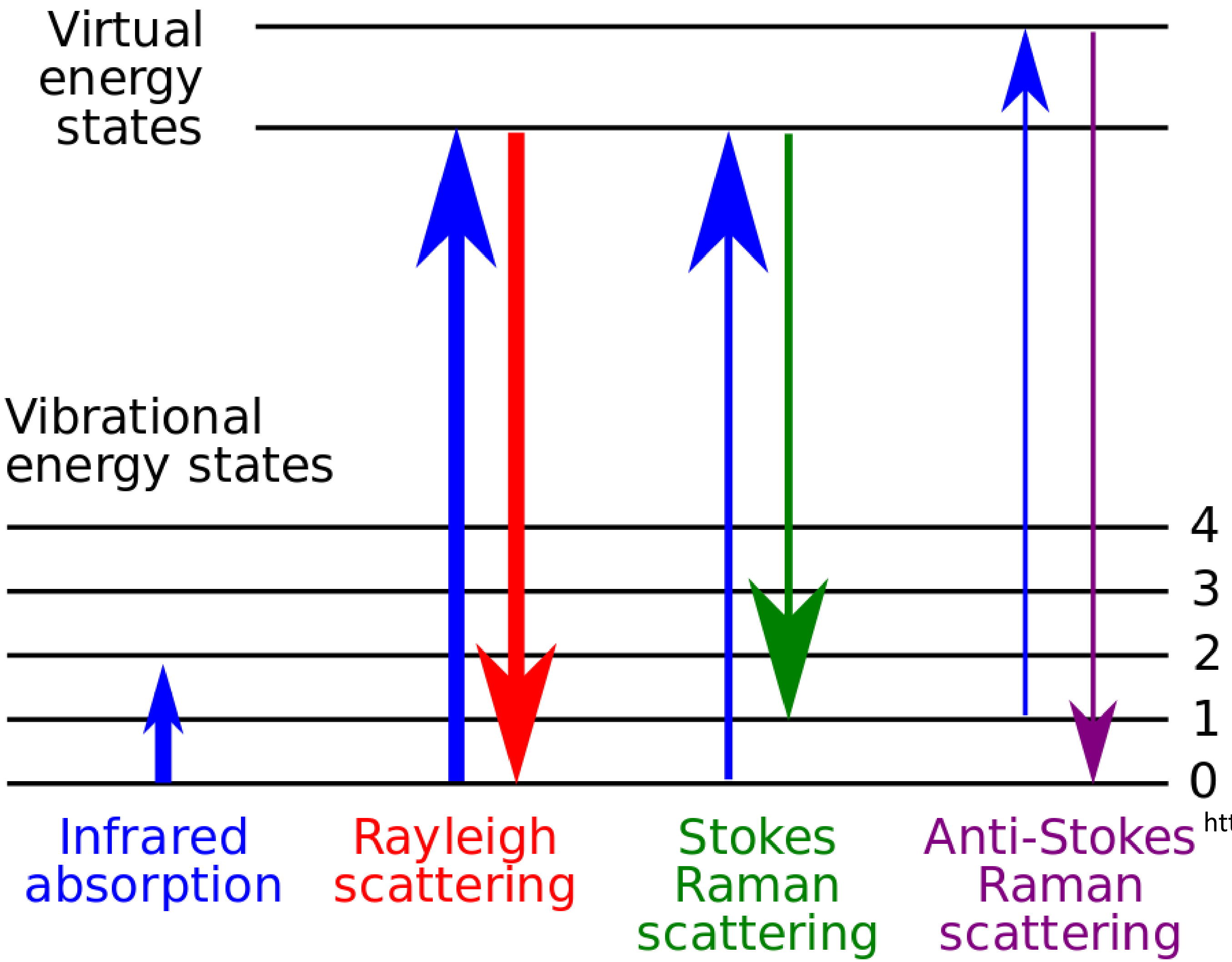


Figure 1-2. Phonon spectrum and density of states (DOS) in cuprous oxide, Cu_2O, calculated at the experimental lattice parameter $a_0 = 4.27$Å. Experimental data on inelastic neutron scattering (Bohnen et al. 2009) and Raman scattering (Yu and Shen 1975) are shown, respectively, as open circles and open squares.

Korzhavyi, P. A., & Johansson, B. (2011). Literature review on the properties of cuprous oxide Cu 2 O and the process of copper oxidation. Swedish Nuclear Fuel and Waste Management Co., Stockholm (Sweden).

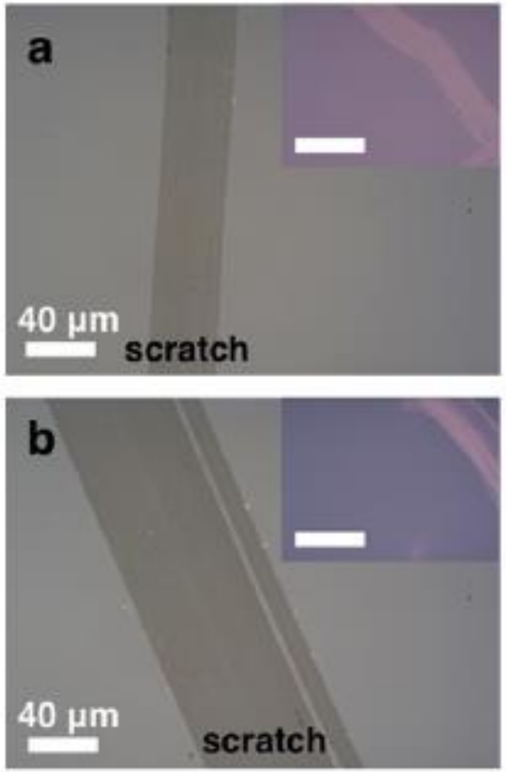
Light/Phonon Interaction



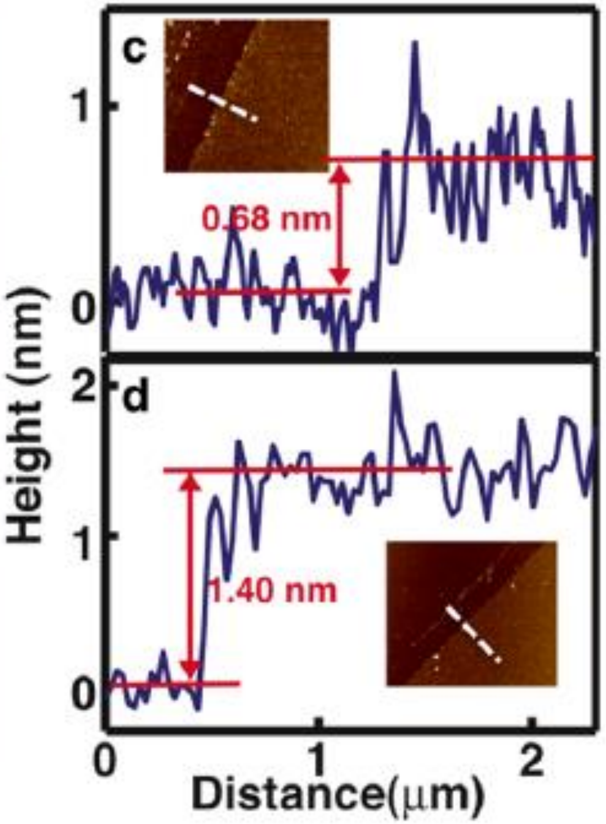
https://en.wikipedia.org/wiki/Raman_spectroscopy

Raman Scattering: Phonon/Photon Inelastic Scattering

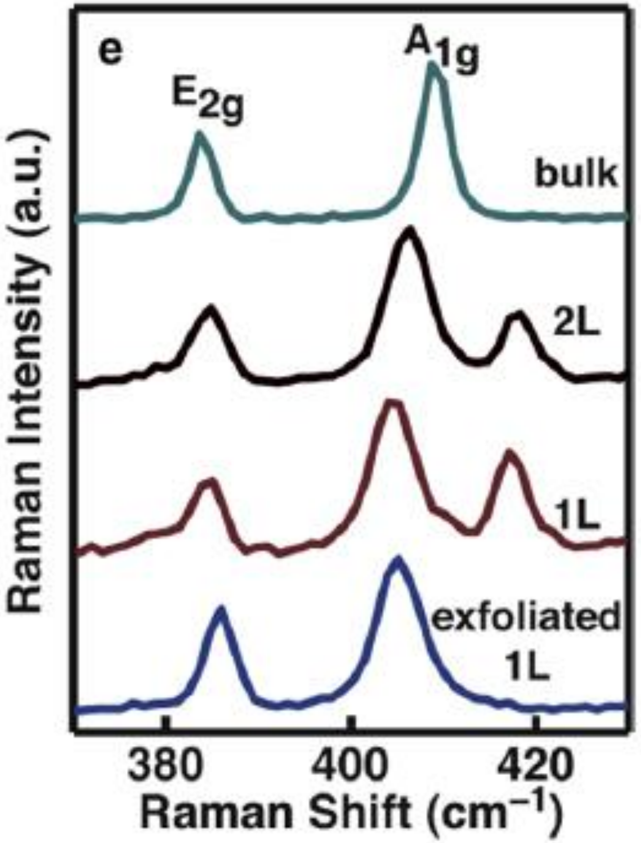
Imaging



Scanning Probe



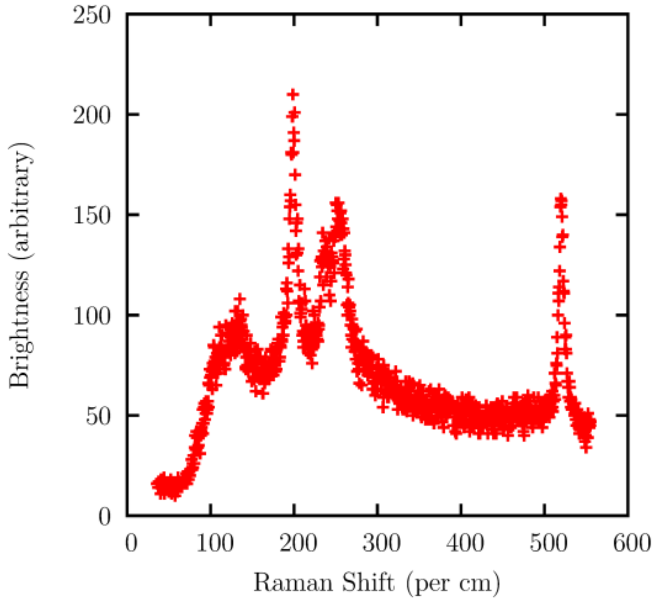
Raman

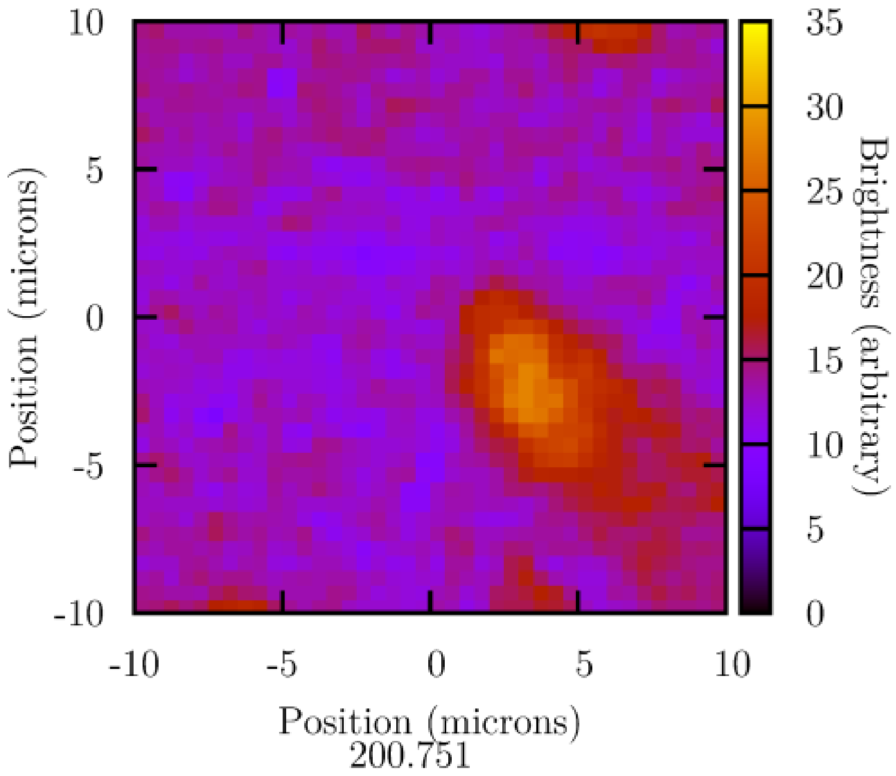


Yu, Yifei, Chun Li, Yi Liu, Liqin Su, Yong Zhang, and Linyou Cao. "Controlled scalable synthesis of uniform, high-quality monolayer and few-layer MoS2 films." Scientific reports 3 (2013).

Raman Benefits

- Fast
- Cost effective
- Structure specific
- Space and time resolution





Titanium Diselenide Flake
Karapetrov Group

Optics of Layered Materials Objectives

- Thickness of thin films can be determined:
    - Reflectance
    - Elipsometry
- Read band diagrams
- Recognize optical properties of direct and indirect bandgap
- Know which experimental technique to use to detect quasiparticles and measure their properties
    - Exciton/Biexciton/Trion luminescence/absorption
    - Time Evolution/Pump Probe
    - Phonon Raman

What could we have discussed but chose not to…

- Heterostructures
- Effective masses
- Harmonic generation and nonlinearities
- Microscopy
- Defects and Grains
- Indirect excitons
- Plasmons
- Water

Snoke, David. "Spontaneous Bose coherence of excitons and polaritons." Science 298.5597 (2002): 1368-1372.