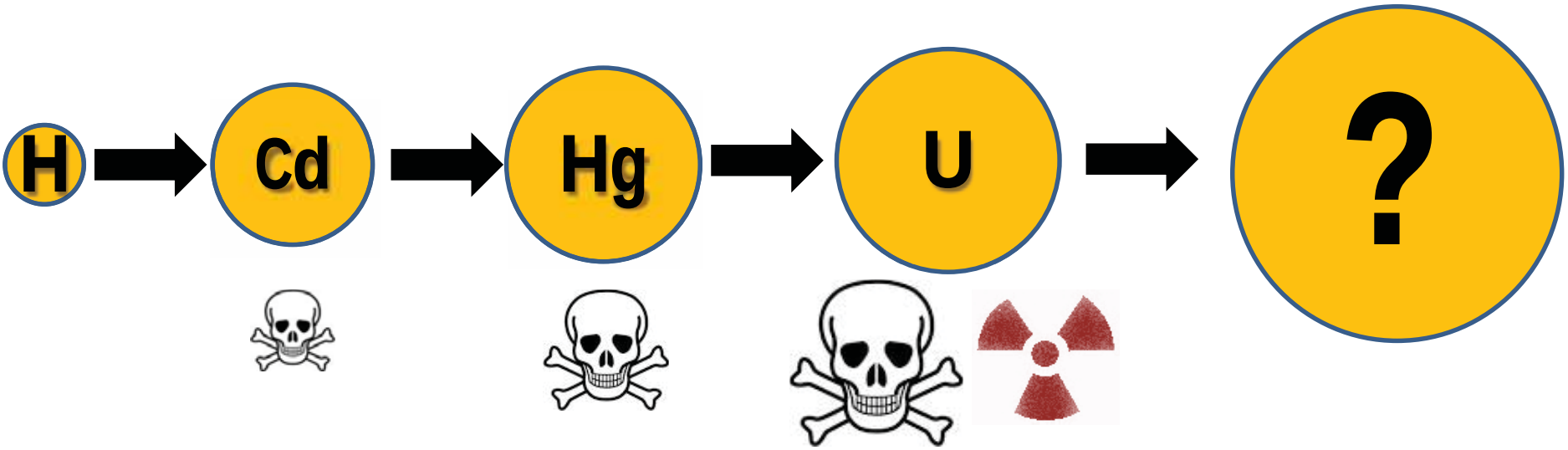


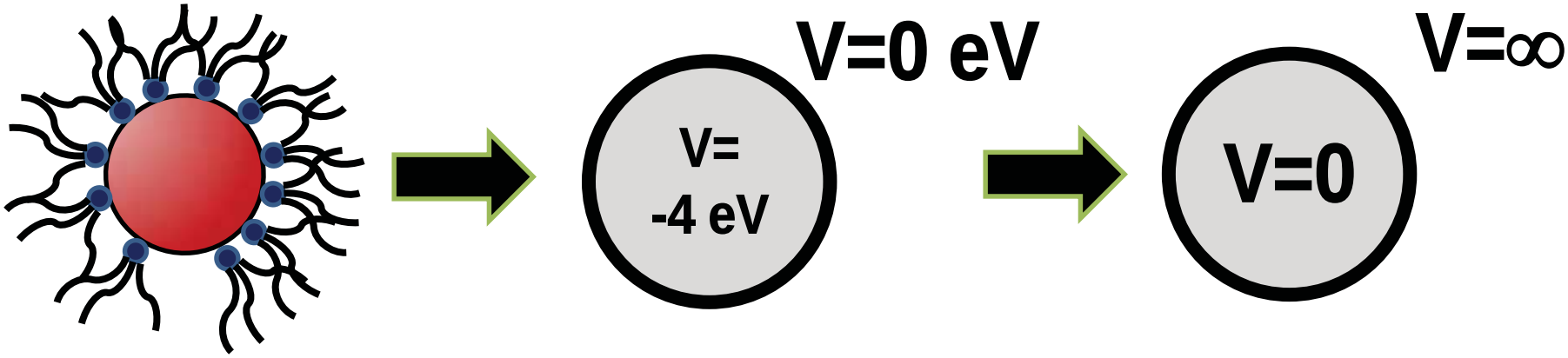
Chemistry with bigger atoms

Anshu Pandey

Solid State and Structural Chemistry Unit

Indian Institute of Science

Quantum Dots: A Coarse-grained view



- Quantum Dot Electronic Structure can be approximated remarkably well as a Spherical Particle in a Box Problem

Quantum Dots: Artificial Atoms

Electrons and holes in a spherical box

- Electronic Wavefunctions:

$1S_e$, $1P_e$, $1D_e$.....$2S_e$, $2P_e$ etc.

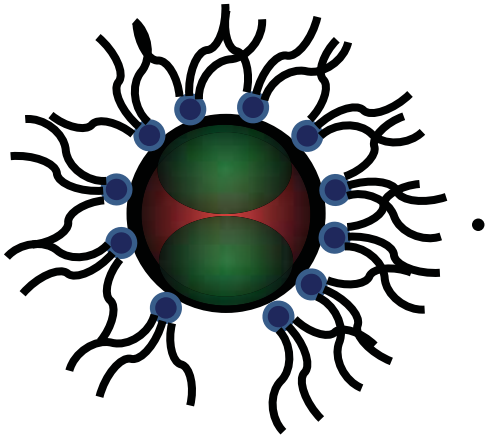
- Hole Wavefunctions:

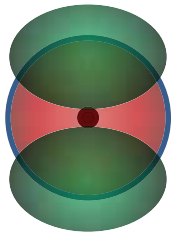
$1S_h$, $1P_h$, $1D_h$.....$2S_h$, $2P_h$ etc.

Looks like hydrogenic orbitals: 1s, 2s, 2p etc.

The term “Artificial Atom” was coined to reflect this similarity.

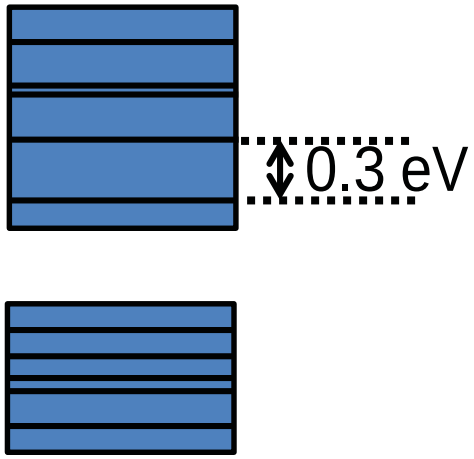
QDs vs Atoms

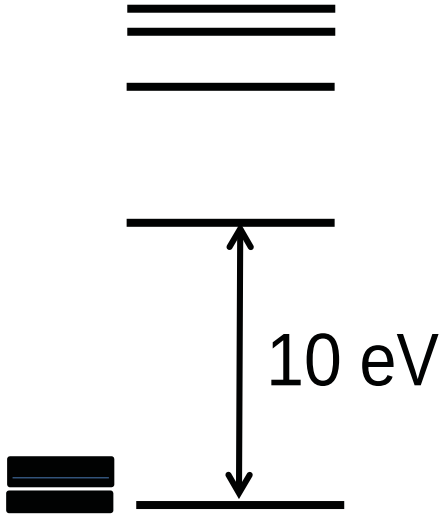




Spatial Extent 10 nm 0.1 nm

Energy Separation between levels



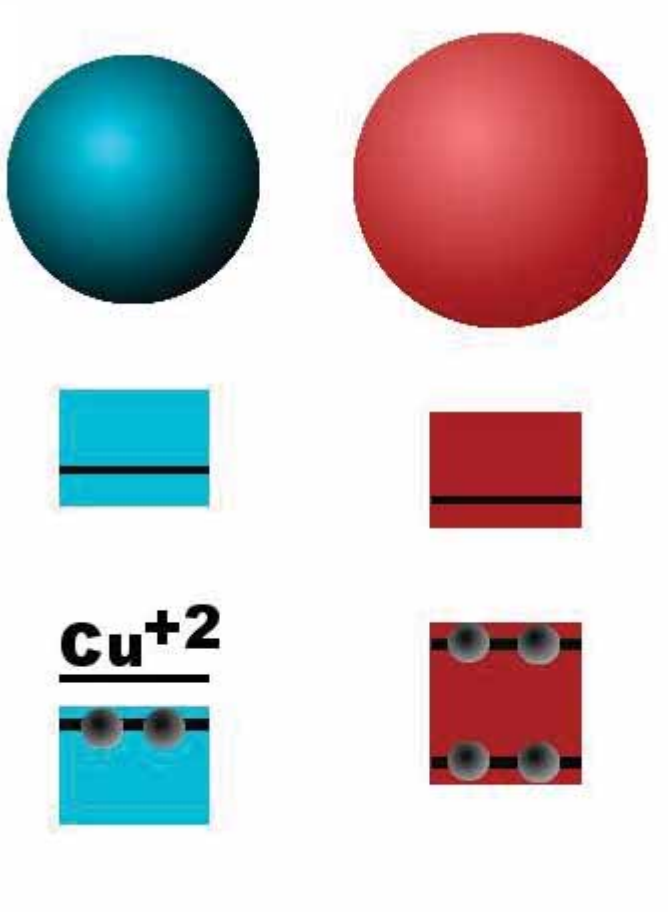


Bringing Chemistry to QDs

- **Introduce a redox active dopant into a redox inert QD**

Rekha M. et. al. JPC C, 118, **30101 (***2014)*

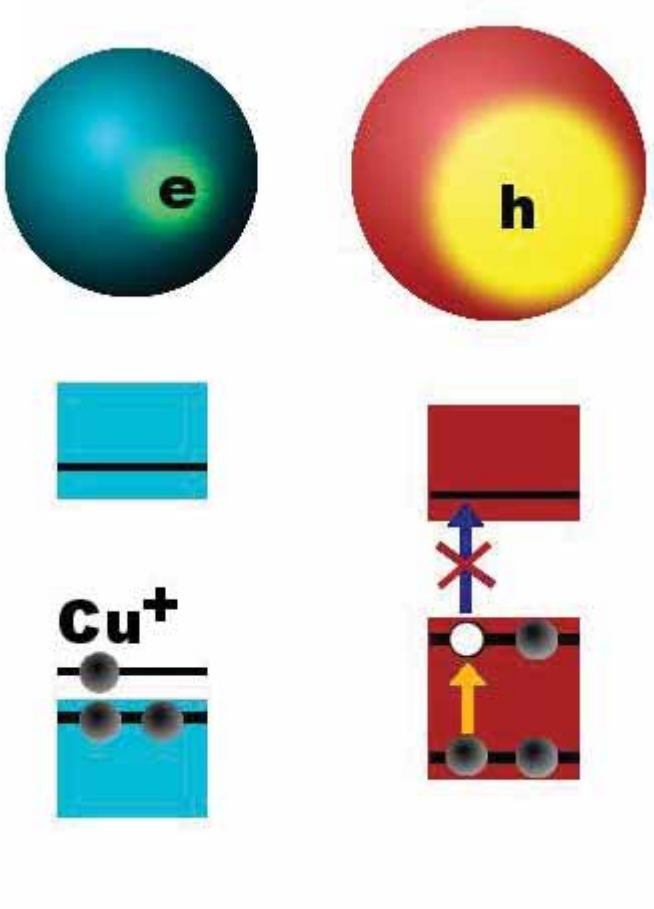
Bringing Chemistry to QDs



- **Put this QD near a redox-active QD**

Rekha M. et. al. JPC C, 118, **30101 (***2014)*

Charge transfer



- Charge is transferred between the QDs
- The transferred charge resides in a quantum confined state

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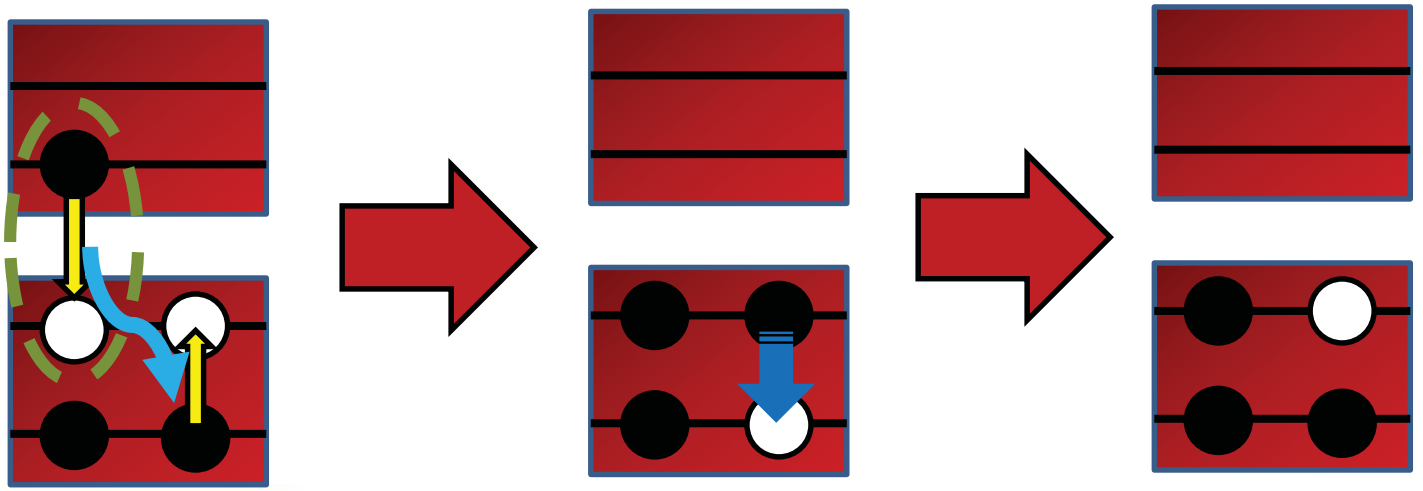
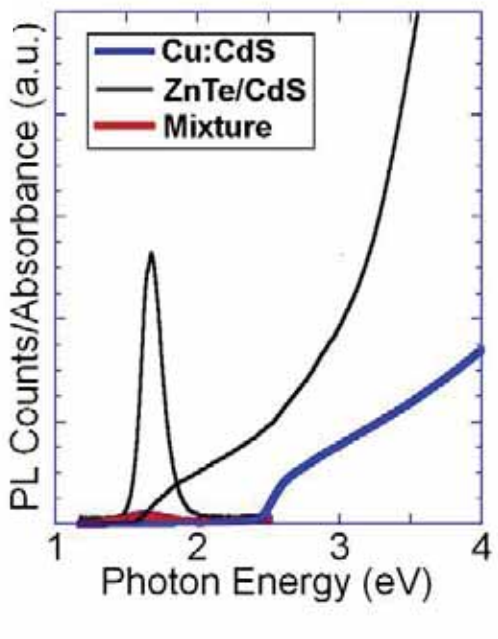
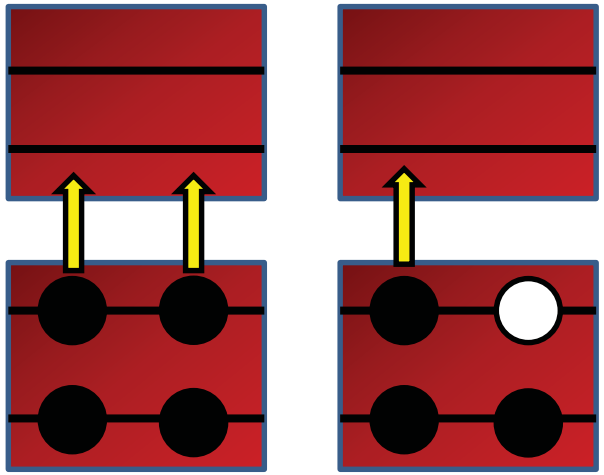
Charge transfer: Signatures



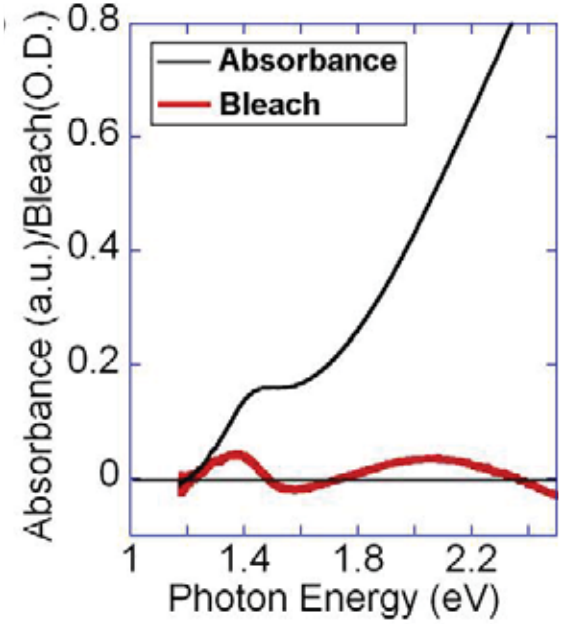


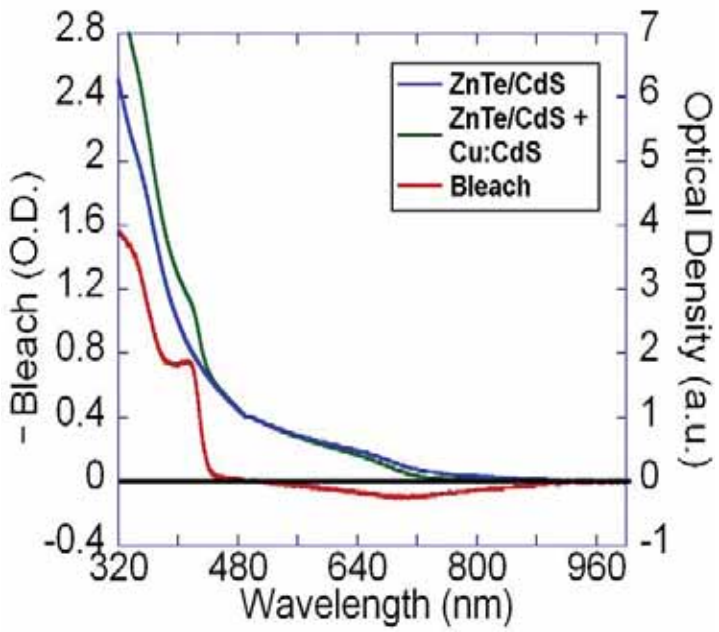
- The spectator hole can quench PL emission via an Auger mechanism
- Both QDs are individually very bright. Together, neither emits.

Bleaching

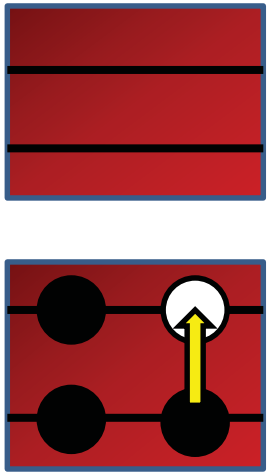


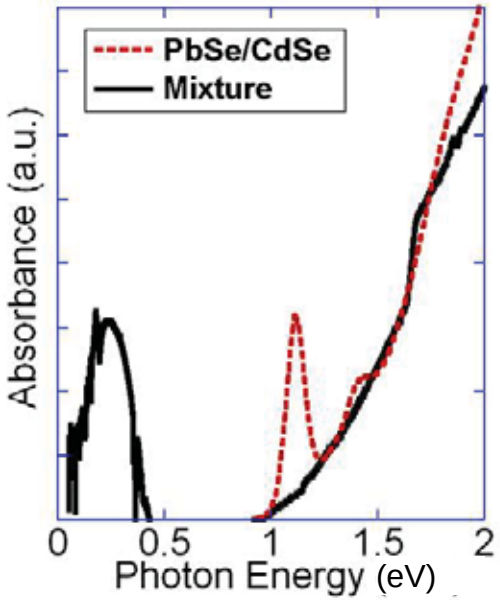
- The formation of a free carrier bleaches absorption
- Absorptions of the two materials are non additive.





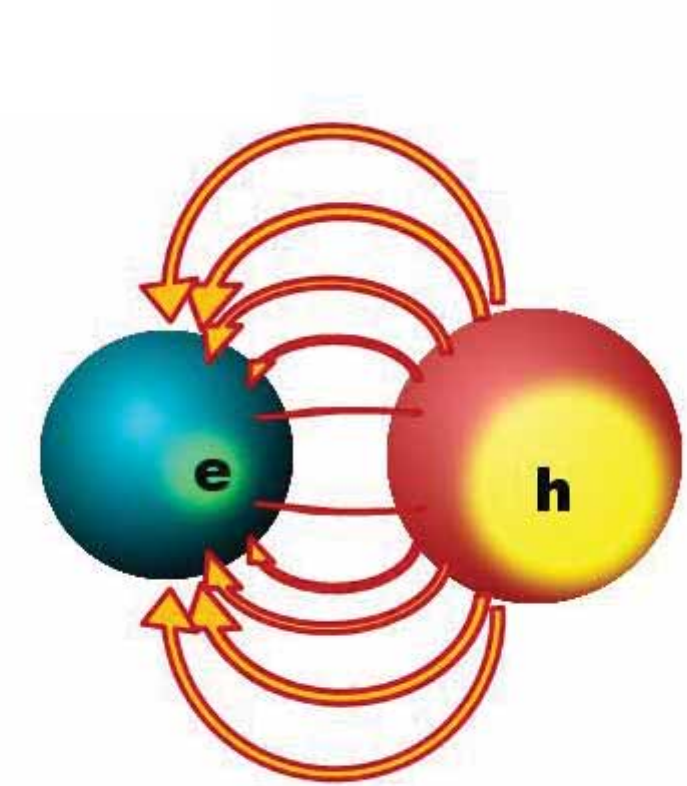
Intraband Absorption





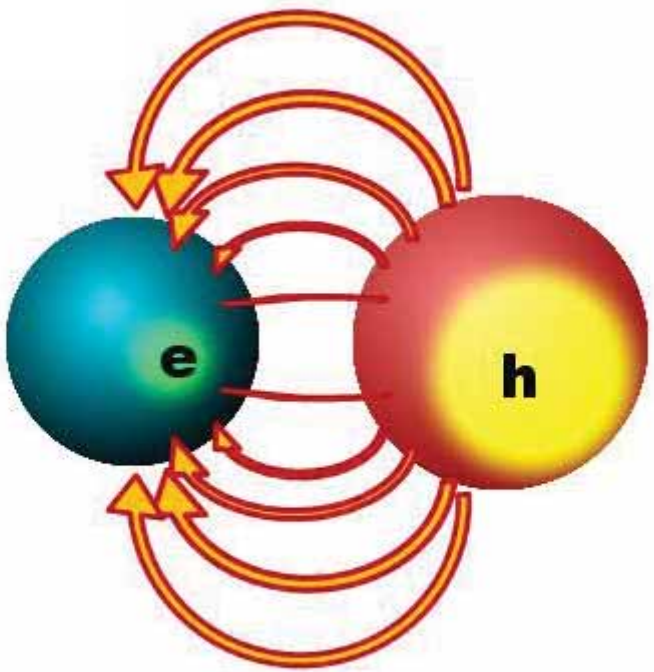
- The most emphatic confirmation for this process comes from the appearance of an intraband absorption in the infrared

Coulomb binding



- Following charge transfer, the two QDs attract each other via coulomb interactions
- Conceptually, this is no different from the ionic bonds that hold together compounds such as NaCl.

Coulomb binding



- Formation of a QD solid held together by coulomb interactions

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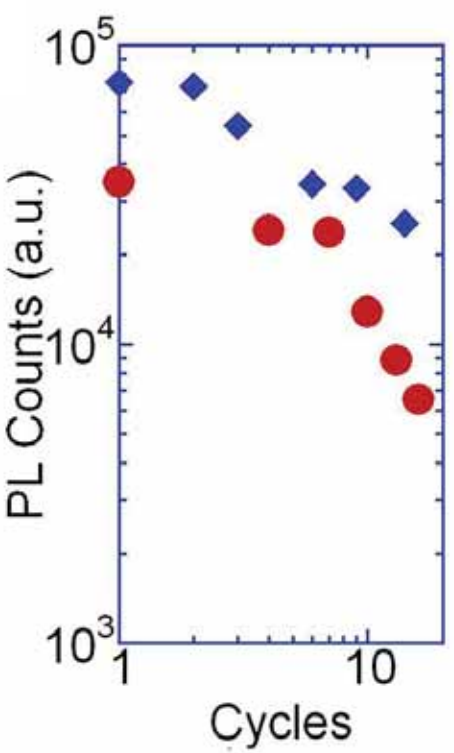
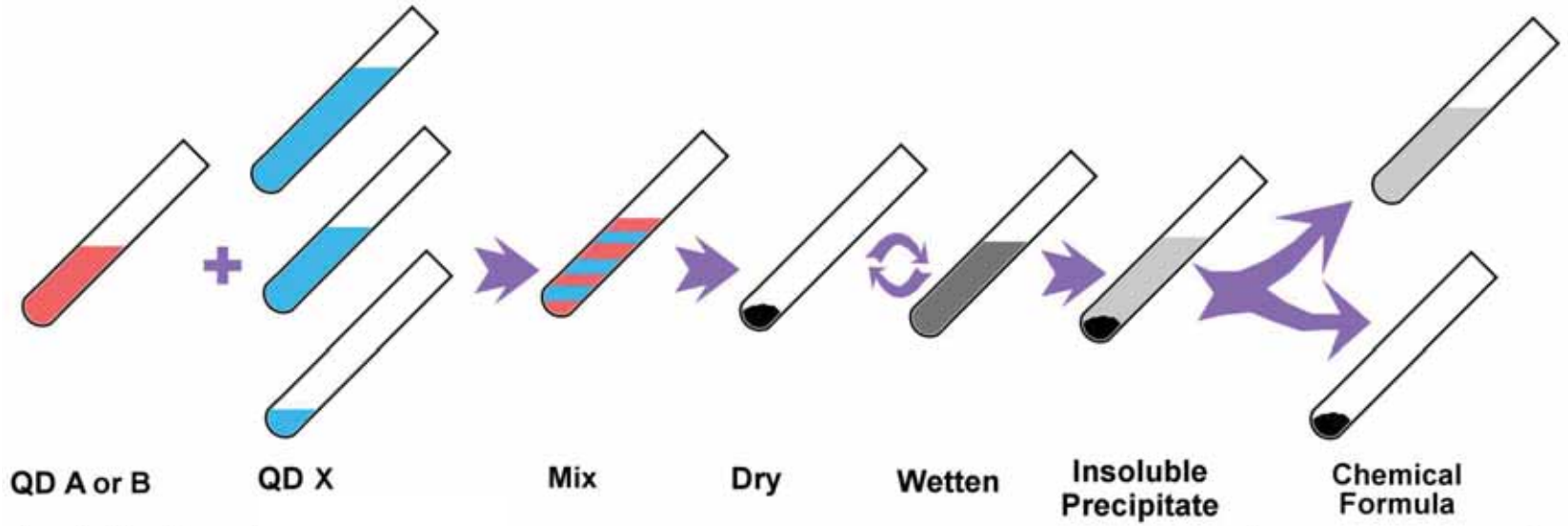
Disordered glassy solids



- The behavior of these materials is typical of a disordered, granular material that evolves in response to each perturbation, but does not reach its energetic minimum.

- Not NaCl, but quite like Sodium Calcium Silicate (soda-lime glass).

This is a chemical transformation



	A	X
i)	1	15
ii)	1	4.2
iii)	1	3.5

A:PbSe/CdSe
B:ZnTe/CdS
X:Cu:CdS

i)	$AX_{1.5}$
ii)	$AX_{1.7}$
iii)	$AX_{2.2}$

The concept of stoichiometry still holds!!!

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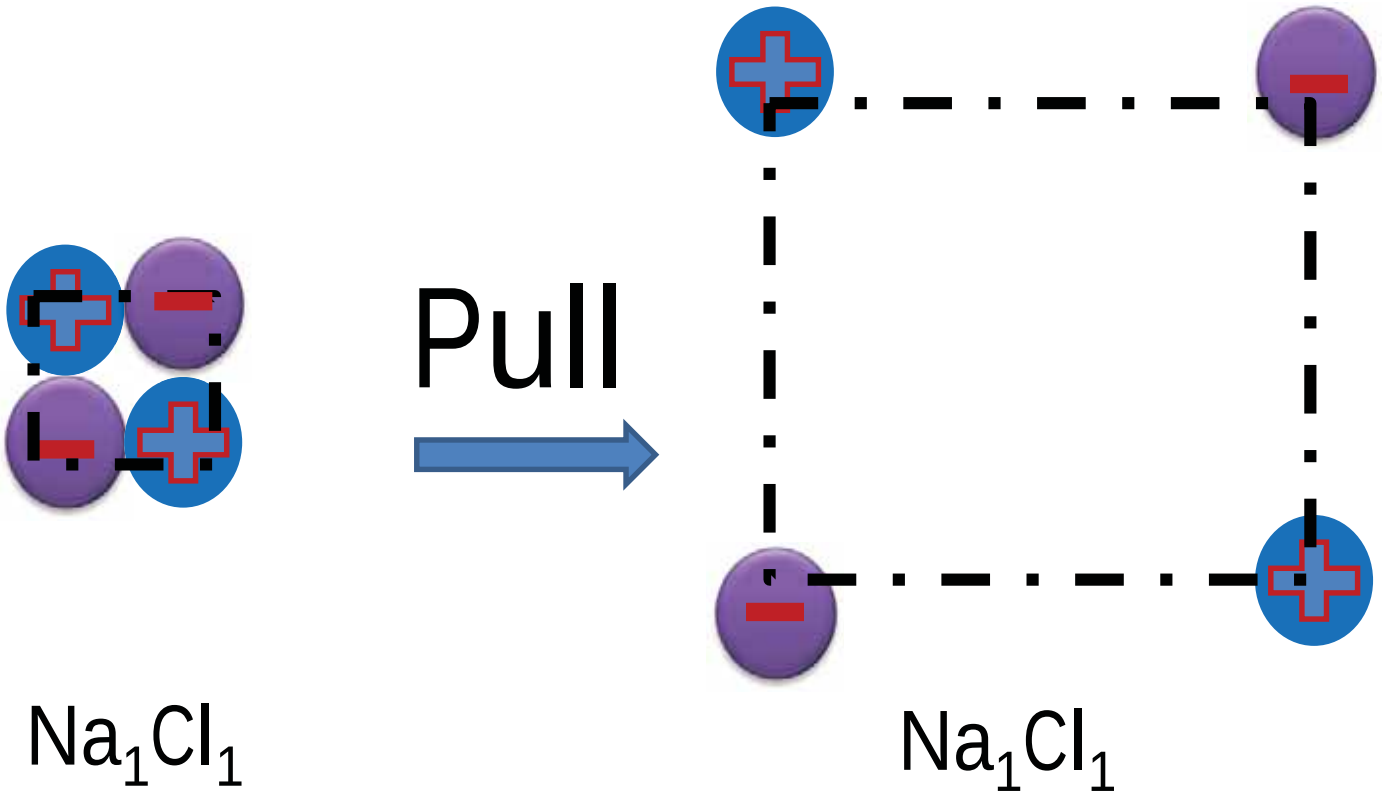
Why are QD-QD solids Stoichiometric

- **Packing Effects**
  - **(Impossible in disordered solids)**
- **Shell Filling**
  - **(Insufficient level separation)**

- Adjacent QD levels are <0.1 eV apart.
- In contrast, atomic oxidation states are separated by ~1 eV
- Creation of a Stoichiometric defect is 10^{12} times easier.

Validating the origins of Stoichiometry

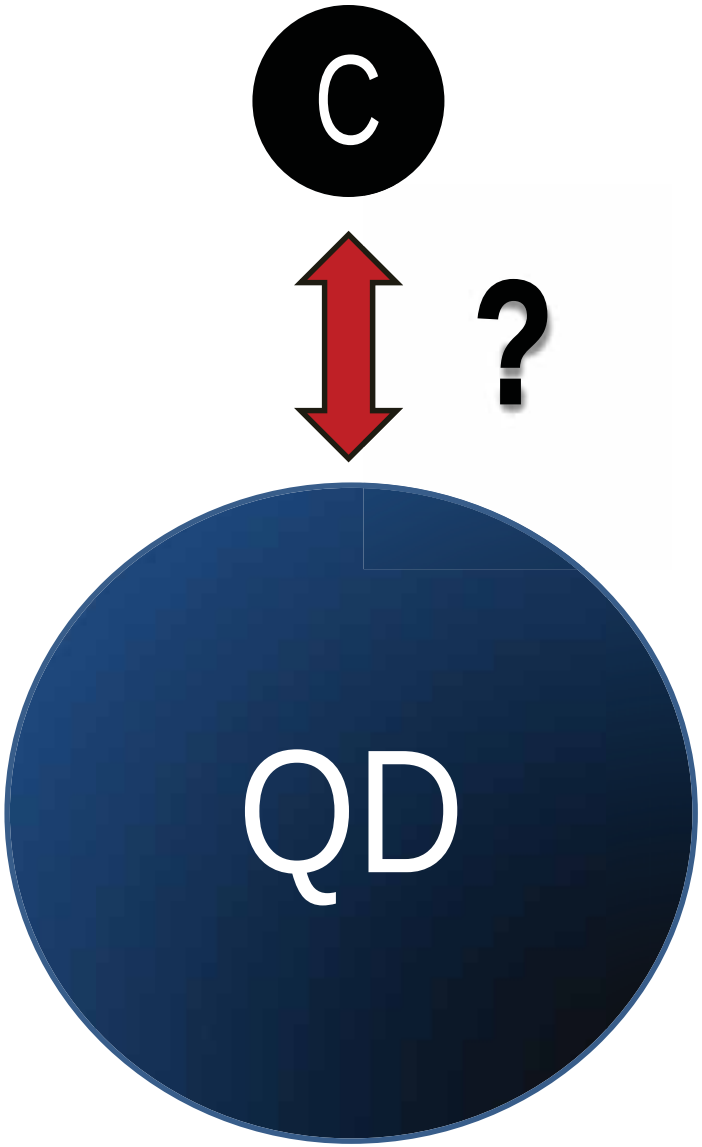


Thought Experiment: continuously increasing the lattice parameter of NaCl

Conclusions

- QDs react the same way as atoms
- This “Chemistry” allows synthesis of stoichiometric compounds
- QDs however lack valence and do not obey the rules of conventional chemistry
- This chemistry though rudimentary, is promising
  - We have observed analogs for:
    - $Na + Cl \rightarrow Na^{+} + Cl^{-}$

Acknowledgements



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