Quantum spectroscopy applied to perovskite nanomaterials

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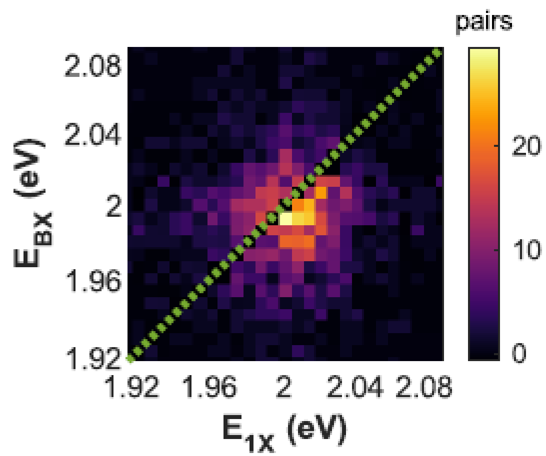
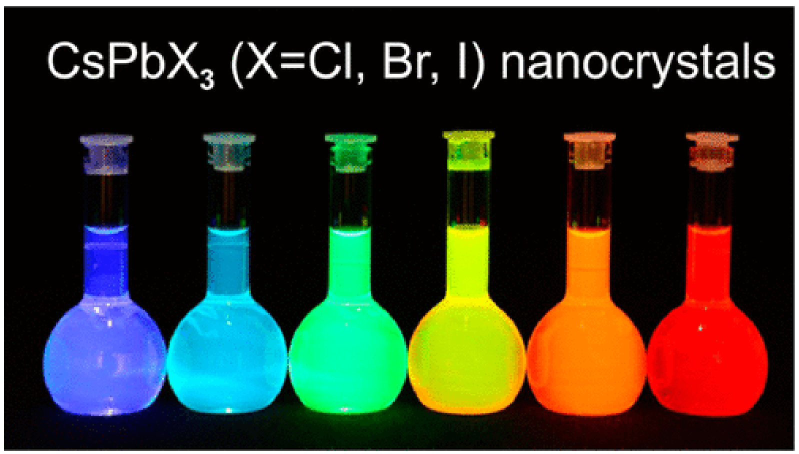


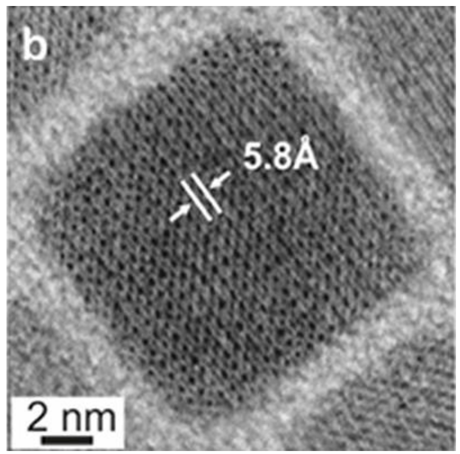
23rd Sede Boqer Symposium, September 2022

Why perovskite nanocrystals?

- Easy to fabricate
- Phase can be stabilized via ligand control
- Possible to study under high fluence
- Possible to study surface interactions

… Interesting proxy also for bulk properties





L. Protescu et al., Nano Lett. 15, 3692 (2015)

Outline

- Reminder on photon correlations
- A few words on detectors
- Some applications of photon correlations in quantum dot spectroscopy

  - Multiexciton spectroscopy by photon statistics

  - Heralded spectroscopy of quantum sources

  - Heralded defocused imaging of biexcitonic dipoles

  - What do we know now about perovskites?

- Conclusion

The Hanbury Brown and Twiss stellar interferometer

HB&T proposed a new kind of telescope to measure the angle subtended by an object in the sky – which does not require a large mirror to resolve the size

1046 NATURE November 10, 1956 Vol. 178

A TEST OF A NEW TYPE OF STELLAR INTERFEROMETER ON SIRIUS

By R. HANBURY BROWN
Jodrell Bank Experimental Station, University of Manchester
AND
Dr. R. Q. TWISS
Services Electronics Research Laboratory, Baldock

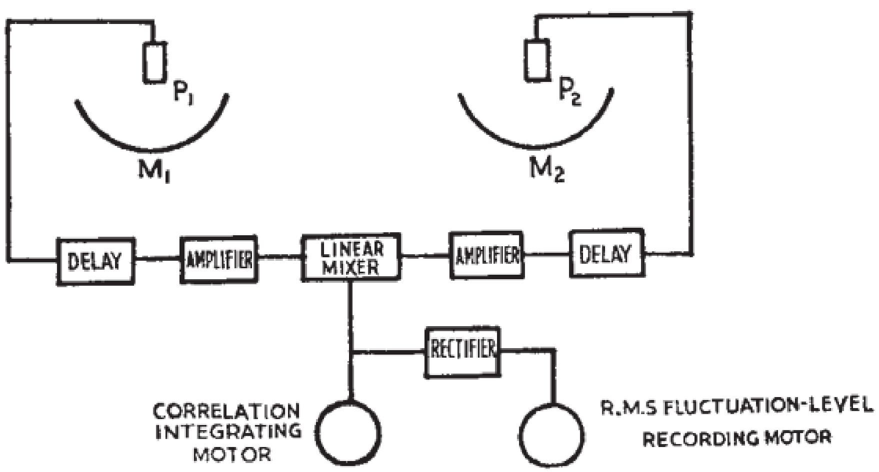


Fig. 1. Simplified diagram of the apparatus

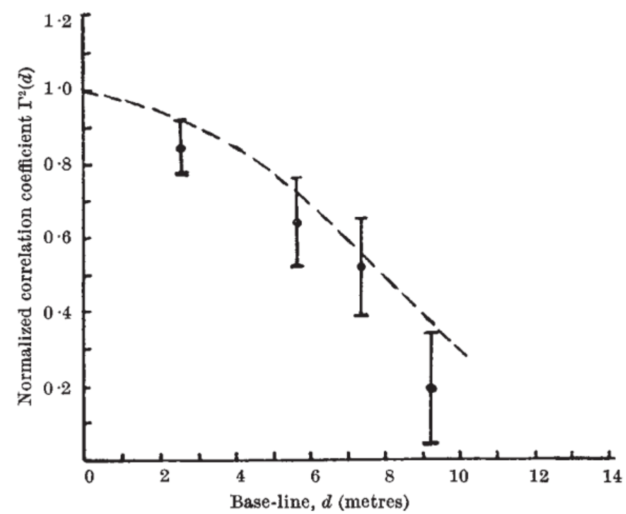


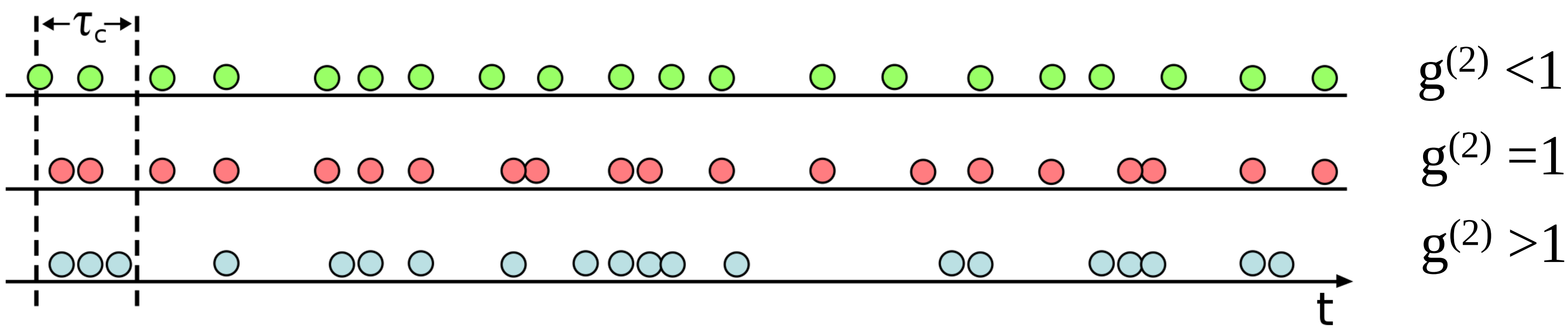
Fig. 2. Comparison between the values of the normalized correlation coefficient $\Gamma^2(d)$ observed from Sirius and the theoretical values for a star of angular diameter 0·0063″. The errors shown are the probable errors of the observations

Photon statistics and photon time distribution

A convenient characteristic of photon statistics is the second order correlation coefficient $g^{(2)}$

$$g^{(2)}(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = \frac{\langle E^*(\mathbf{r}_1, t_1) E^*(\mathbf{r}_2, t_2) E(\mathbf{r}_1, t_1) E(\mathbf{r}_2, t_2) \rangle}{\left\langle |E(\mathbf{r}_1, t_1)|^2 \right\rangle \left\langle |E(\mathbf{r}_2, t_2)|^2 \right\rangle}$$

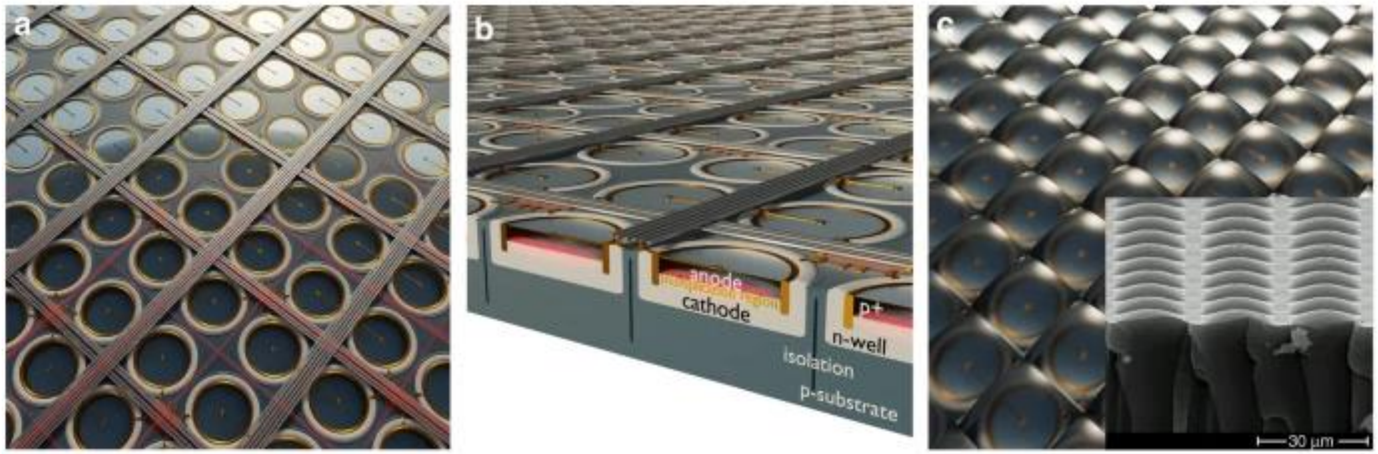
For which we only consider the temporal degree of freedom



Photon detections as function of time for a) antibunched, b) random, and c) bunched light

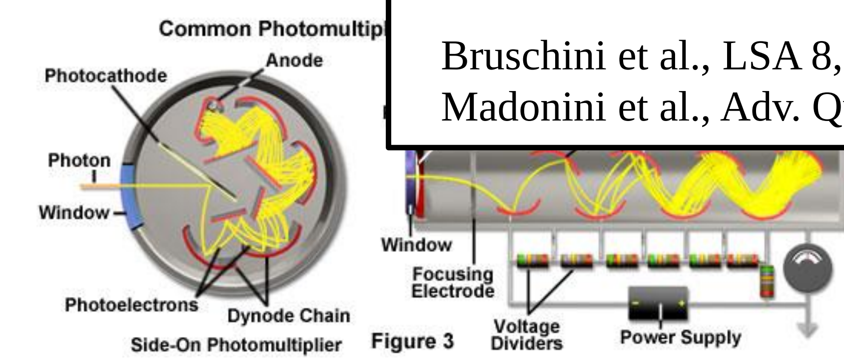
$g^{(2)} < 1$ is a sufficient condition for nonclassicality!

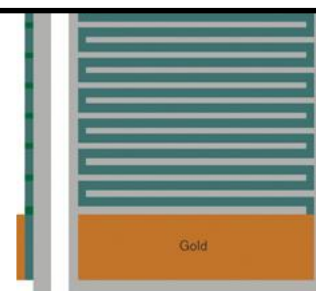
How do we detect single photons?

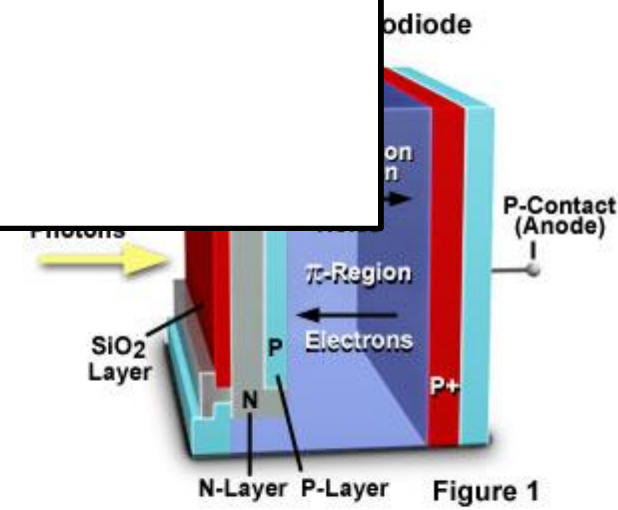


There’s a new kid on the block – monolithic SPAD array imaging sensors

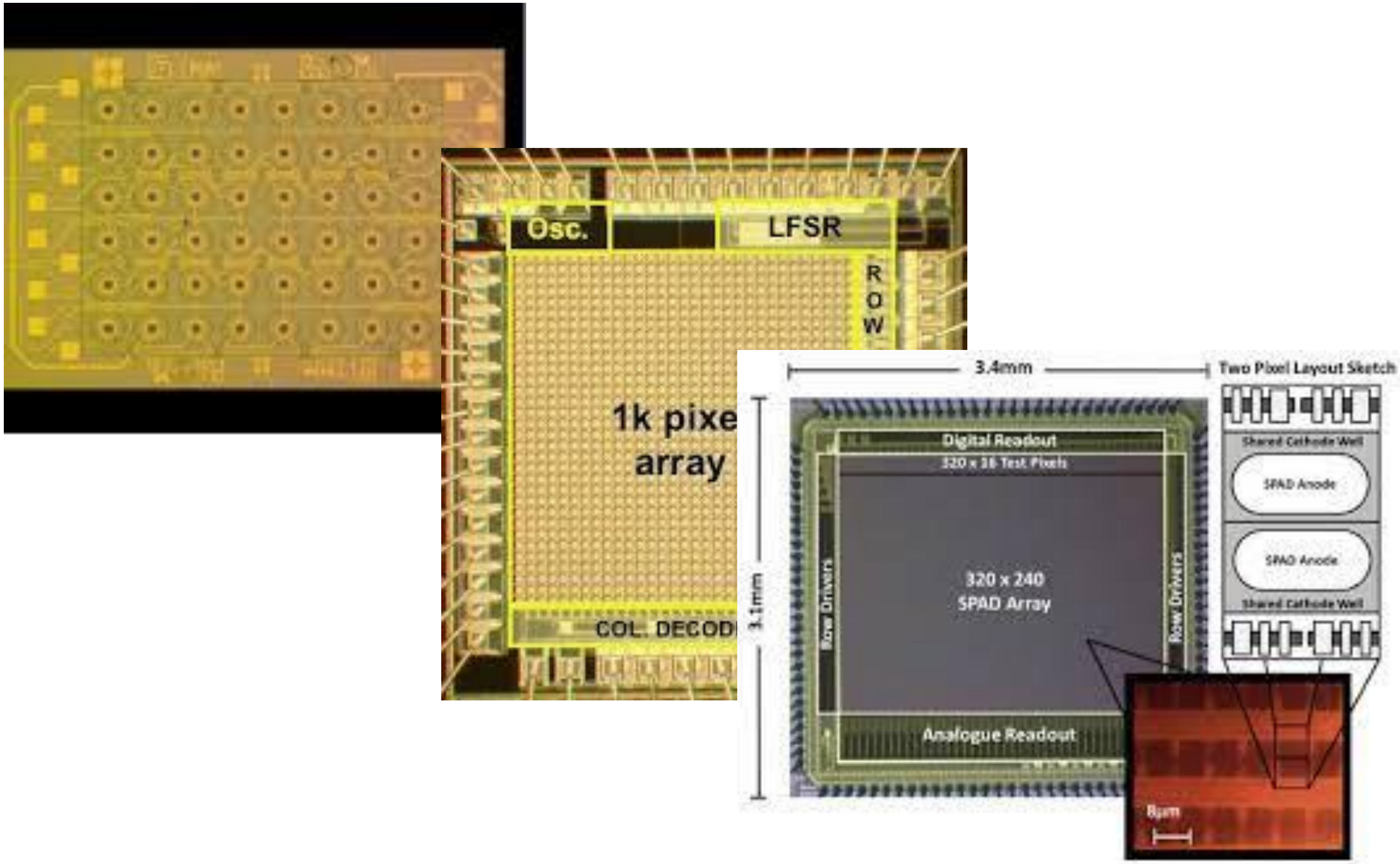
Bruschini et al., LSA 8, 87 (2019)
Madonini et al., Adv. Quantum Tech. 4, 2100005 (2021)







Evolution of SPAD arrays

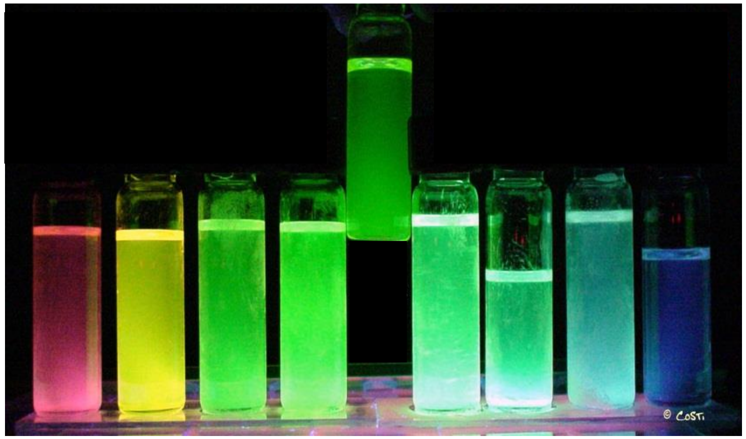


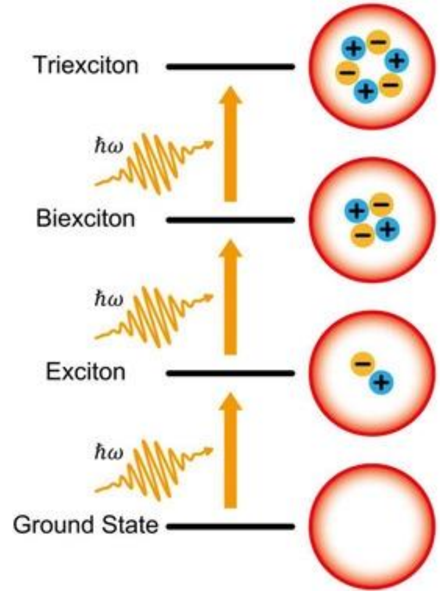
Now at 1Mpixels …
and counting

Why is this important for QD spectroscopy?

CdSe nanocrystal solutions

d=6nm ← d=2nm



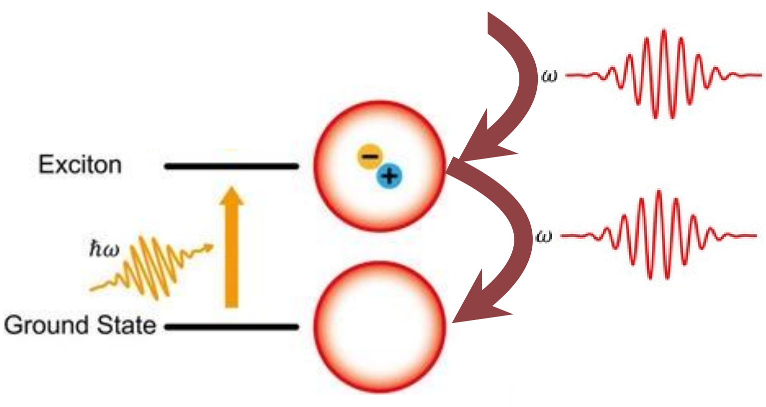


When measuring fluorescence from QDs we are usually interested in emission from the lowest excited state…

but unlike molecular dyes, QDs can support multiexcitons

Multiexcitons are much harder to study because:
(1) they are typically dim emitting states
(2) their emission appears on top of a bright lowest state emission
(3) There are other 'interfering' states

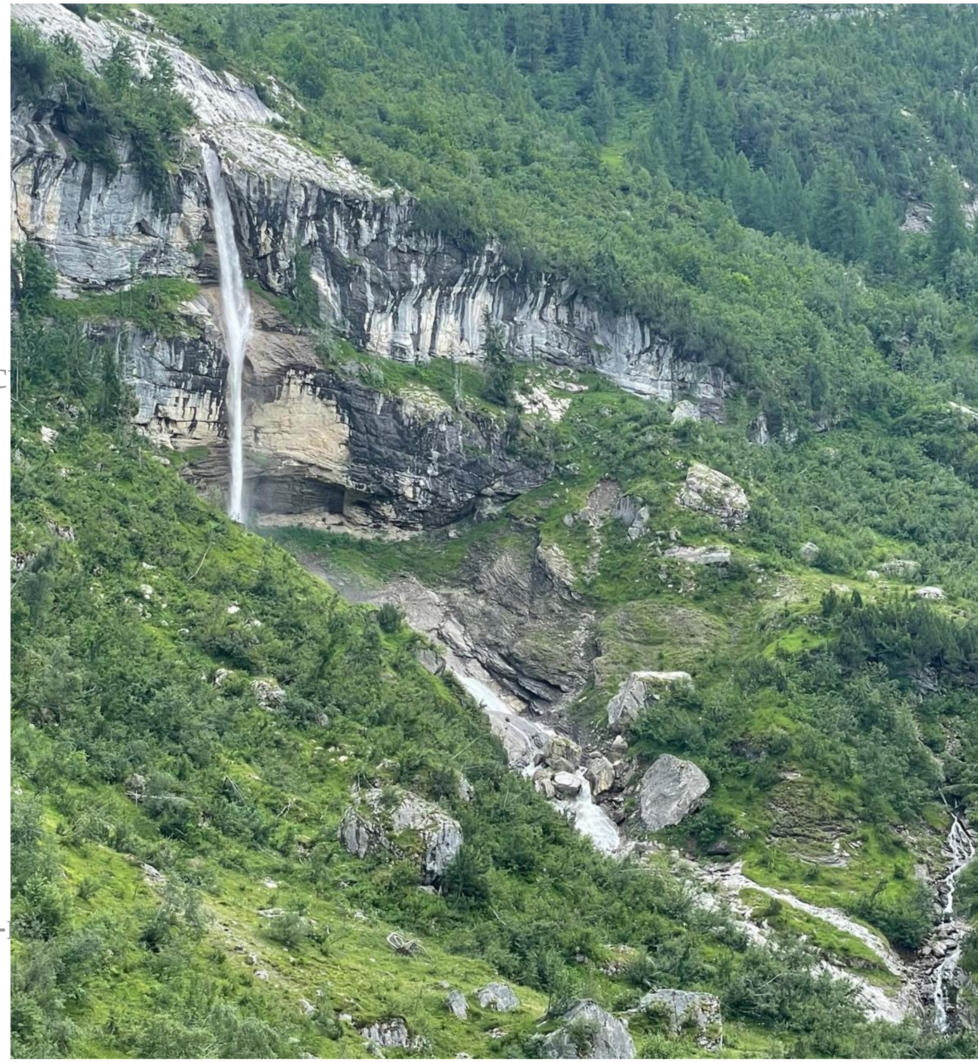
Why is multiexciton spectroscopy hard



Visualization:
Tahara *et al.*, *ChemNanoMat*, *5.8* (2019)
GL *et al.*, *Nano Letters 21.16 (2021)*
Kiselev, *Univ. Jena*, Thesis (2013)

Spec

Non-

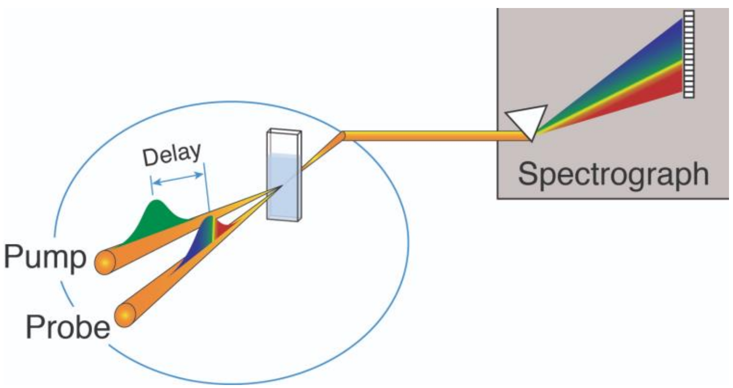


Cascaded emission is easy to separate in the time domain…

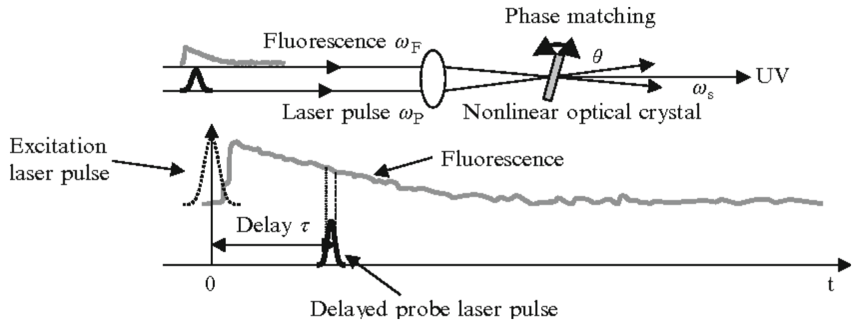
‘Common’ multiexciton spectroscopy methods

Need to resolve both temporal and spectral data

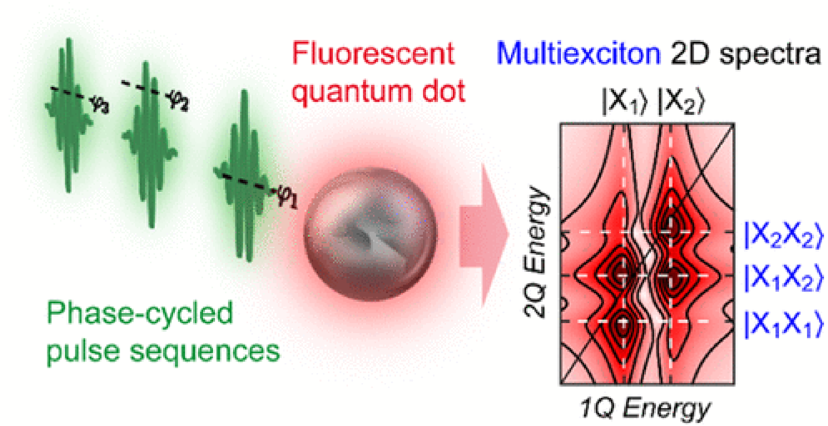
Transient absorption



Transient PL



Multidimensional spectroscopy



But all these are ensemble measurements, averaging over temporal and inter-QD heterogeneity!

Why single nanoparticles

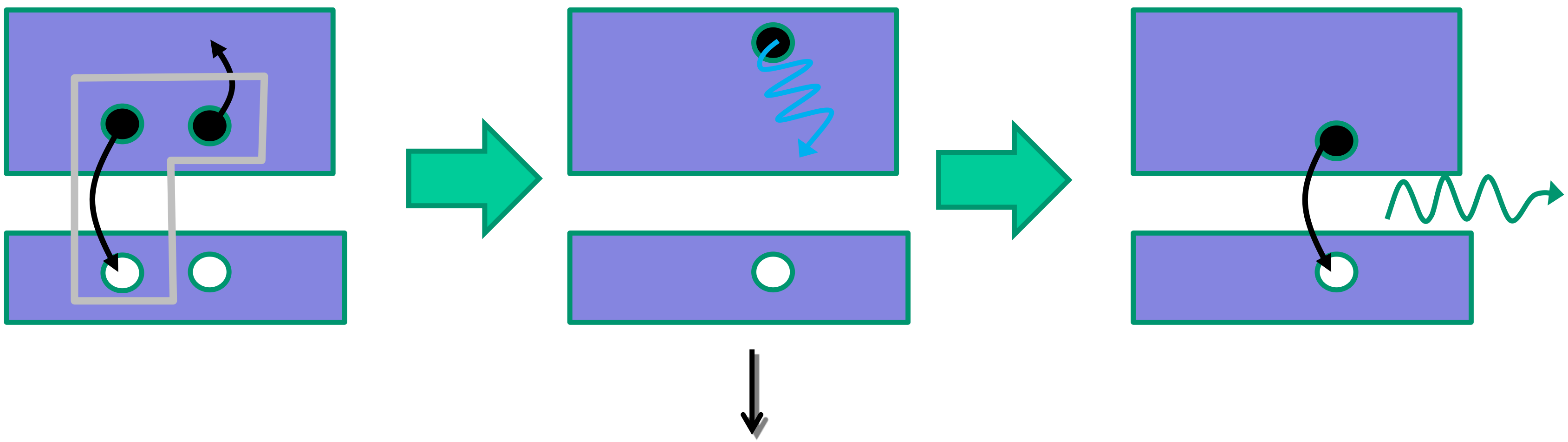
- Local measurements
- Overcoming inhomogeneous broadenings
- Quantum nature of light emission

How?

- Scattering (very hard, scales as V^2)
- Absorption (hard, scales as V but small)
- Photoluminescence (easy, background free)

From Auger recombination to photon statistics

Auger Recombination

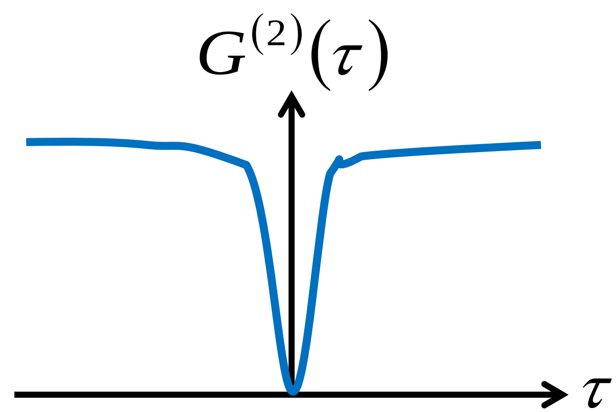


Photon Anti-Bunching

Intensity Correlation

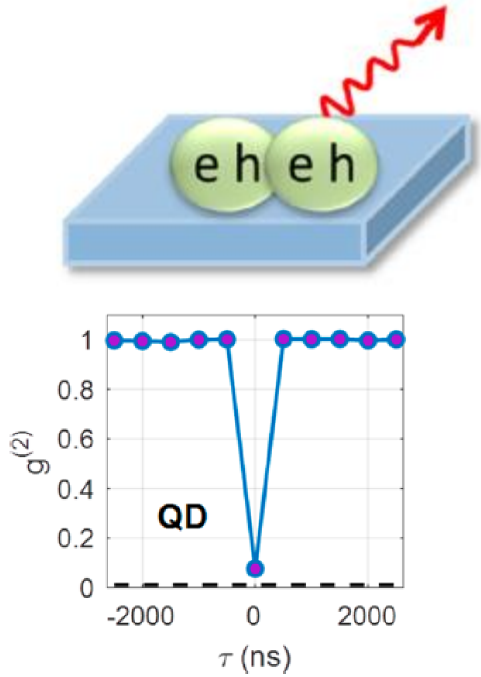
$$G^{(2)}(\tau) = \langle I(t) I(t+\tau) \rangle$$

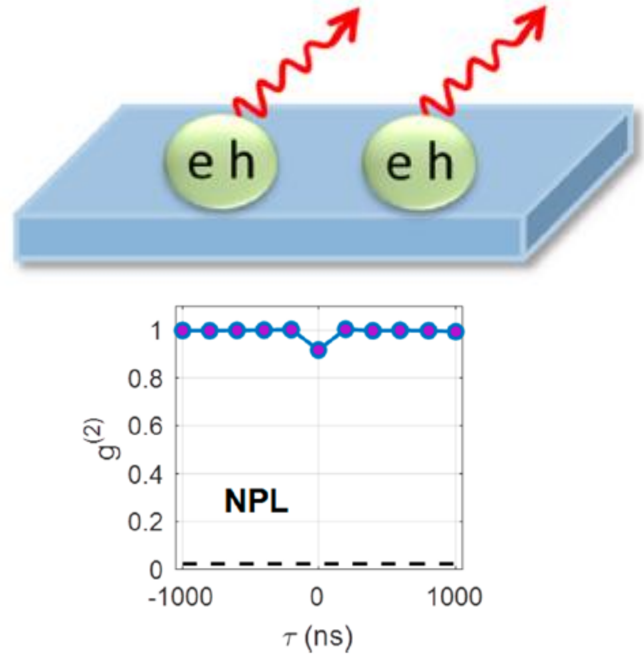
Reduced quantum fluctuations



Quantum spectroscopy

Can we replace ‘traditional’ spectroscopy with photon statistics?



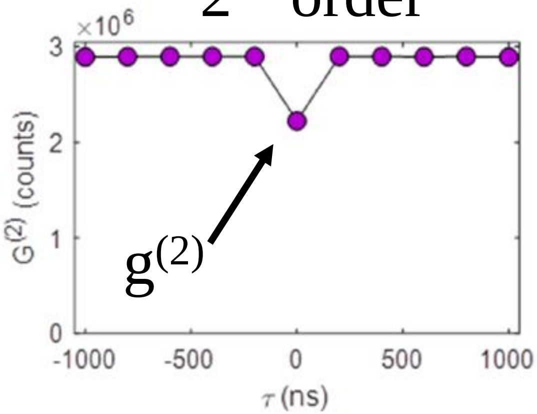


In larger nanocrystals (e.g. nanoplatelets) antibunching is not complete.
Is there information in the higher order photon correlations?

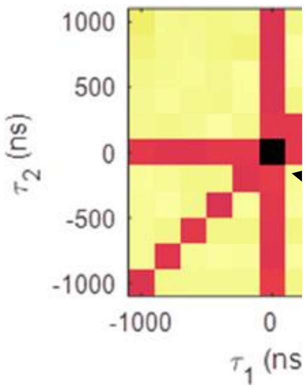
The short answer is “Yes” (resembling 2D spectroscopy)…

Higher order antibunching spectroscopy

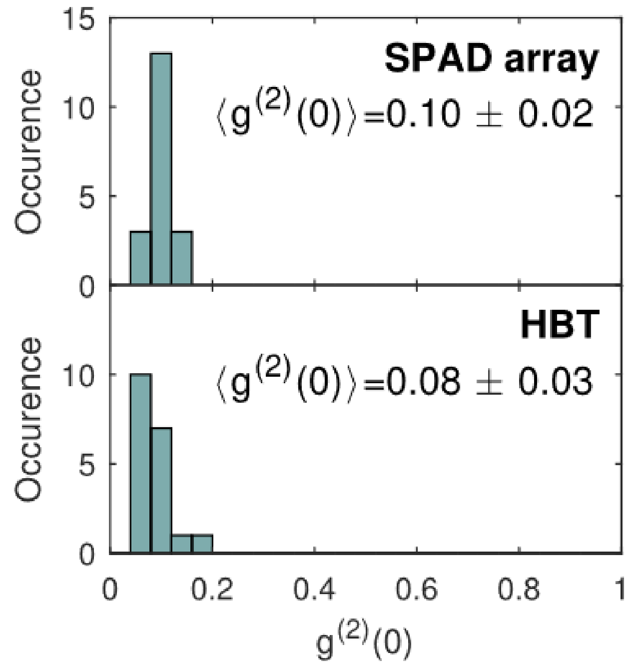
2nd order

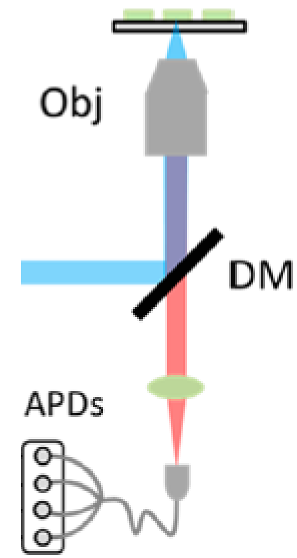


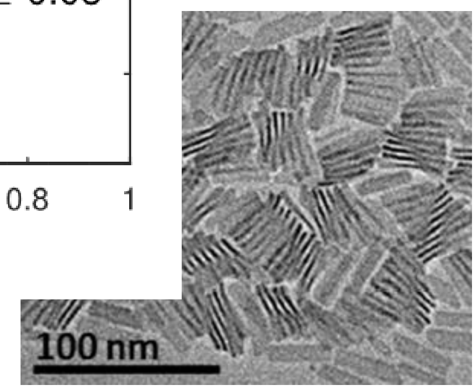
3rd or



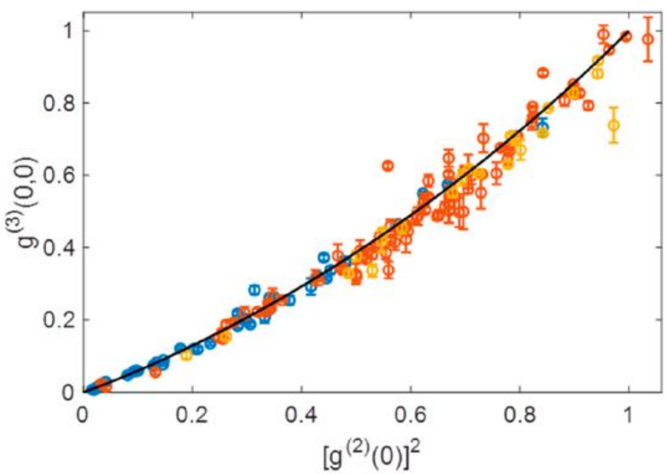
Can also be done with SPAD arrays

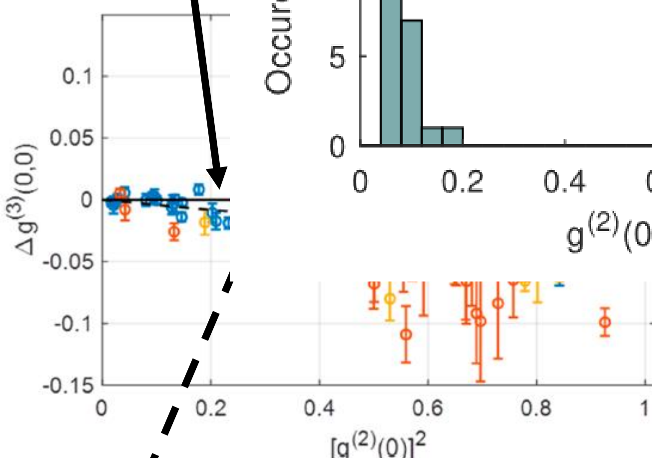






Two body inte





With three body correction

D. Amgar, DO, et al., Nano Lett. 19, 8741 (2019) ; G. Lubin, DO et al., Optics Express 27, 32863 (2019)

Heralded multiexciton spectroscopy

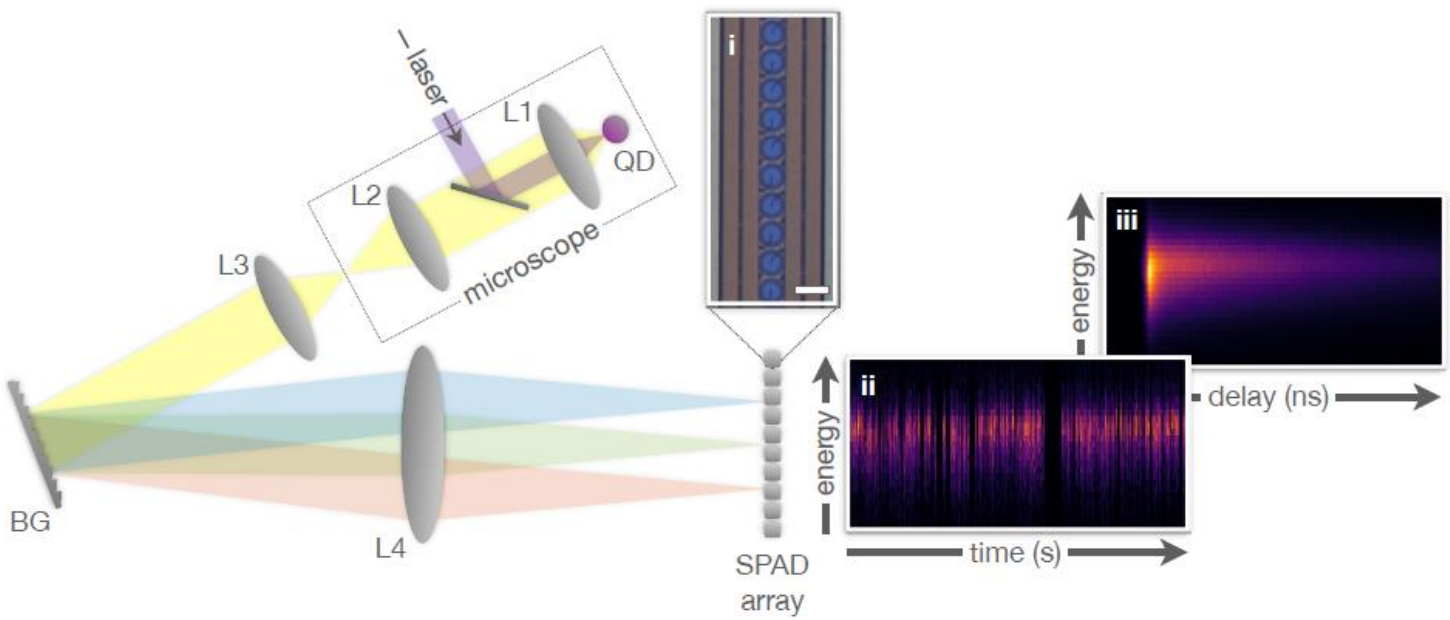
But in performing photon statistics experiments we had to give something up …

we have lost all spectral information!

Is there a way around this?

Heralded multiexciton spectroscopy

New technologies such as monolithic arrays of single photon spectrometers can provide access to previously unexplored properties at the single particle level



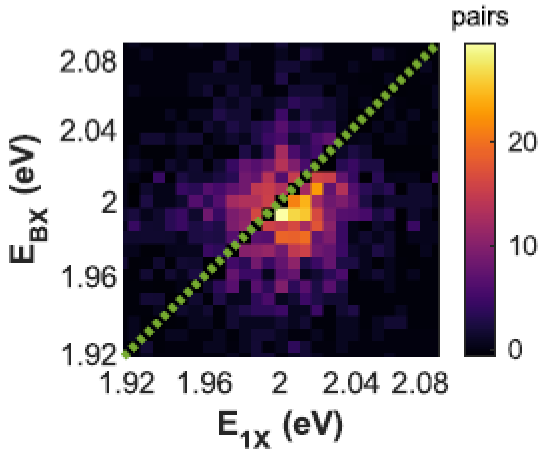
Single-photon time resolved spectrometer based on a 1D SPAD array: ~1ns time resolution, 2nm spectral resolution - simultenaously

G. Lubin, DO, et al., Nano Lett. 21, 6756 (2021)

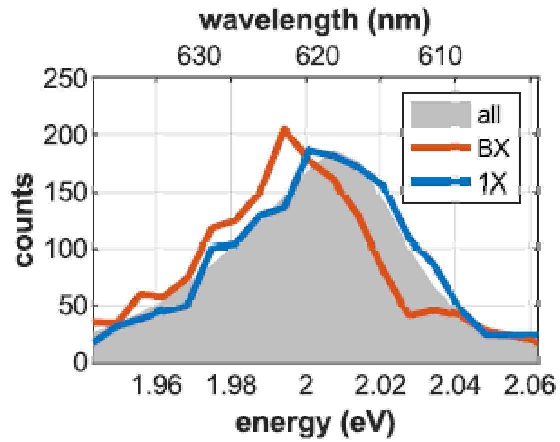
Heralded multiexciton spectroscopy

This enables to identify photon pairs emitted following a single excitation cycle and post-select only events involving a pair of photons (BX-X cascaded emission)

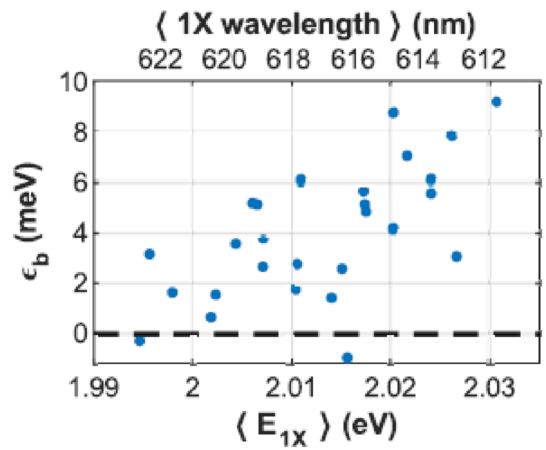
First photon



Second photon



This reveals “hidden” inhomogeneous broadening



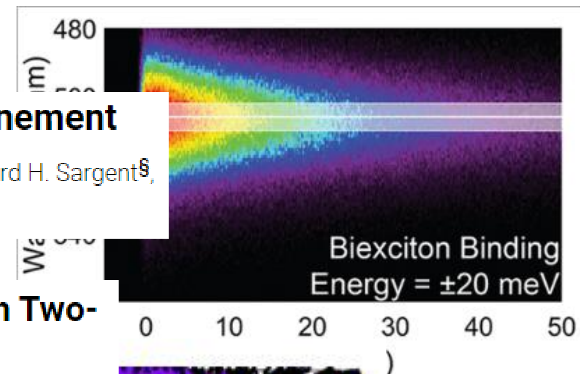
G. Lubin, DO, et al., Nano Lett. 21, 6756 (2021)

An ‘easy’ solution to problems which are not so easy to solve on an ensemble level

What is the biexciton binding energy in a $CsPbBr_3$ perovskite nanocrystal?

Setting an Upper Bound to the Biexciton Binding Energy in $CsPbBr_3$ Perovskite Nanocrystals

Katherine E. Shulenberger, Matthew N. Ashner, Seung Kyun Ha, Franziska Krieg, Maksym V. Kovalenko, William A. Tisdale*, and Moungi G. Bawendi*



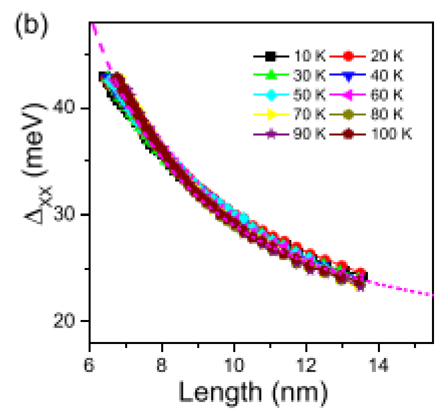
Efficient Biexciton Interaction in Perovskite Quantum Dots Under Weak and Strong Confinement

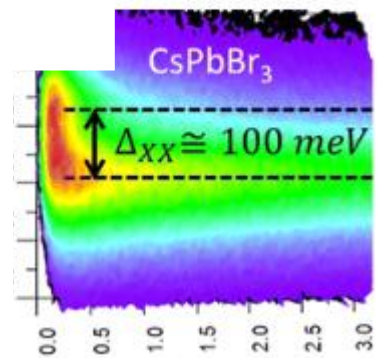
Juan A. Castañeda[†], Gabriel Nagamine[†], Emre Yassitepe[‡], Luiz G. Bonato[‡], Oleksandr Voznyy[§], Sjoerd Hoogland[§], Ana F. Nogueira[‡], Edward H. Sargent[§], Carlos H. Brito Cruz[†], and Lazaro A. Padilha[*†]

Inhomogeneous Biexciton Binding in Perovskite Semiconductor Nanocrystals Measured with Two-Dimensional Spectroscopy

Xinyu Huang, Lan Chen, Chunfeng Zhang*, Zhengyuan Qin, Buyang Yu, Xiaoyong Wang, and Min Xiao*

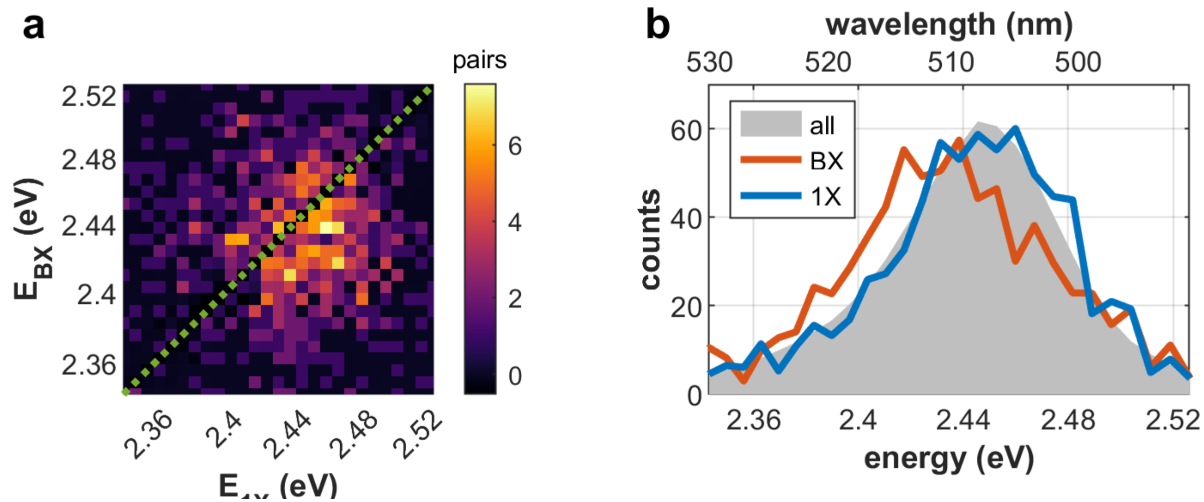
# of answers = # of methods used in the measurement …





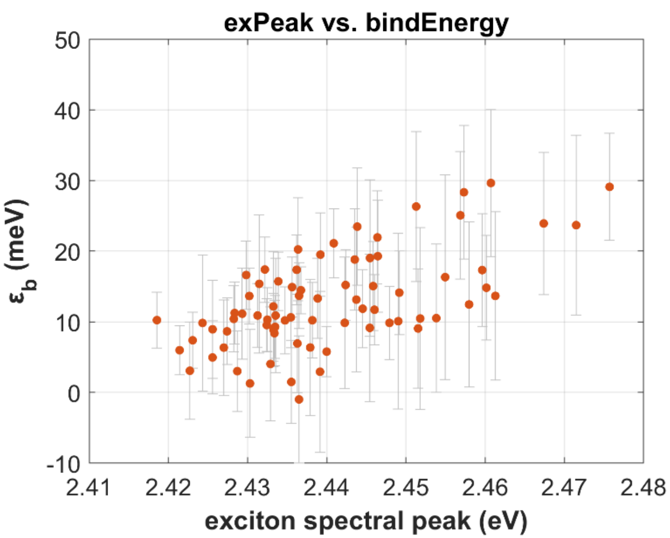
An ‘easy’ solution to problems which are hard To solve on an ensemble level

Heralded spectroscopy provides an unambiguous answer for every particle



$BX_{peak} \approx 2.4335\ eV$ $\quad 1X_{peak} \approx 2.4491\ eV$

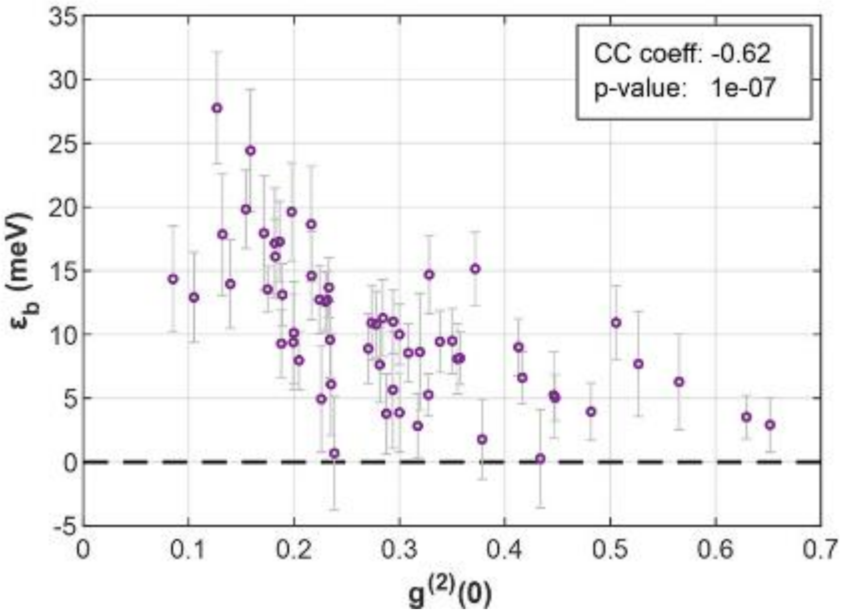
$$\varepsilon_b = 15.6 \pm 3.6\ meV$$

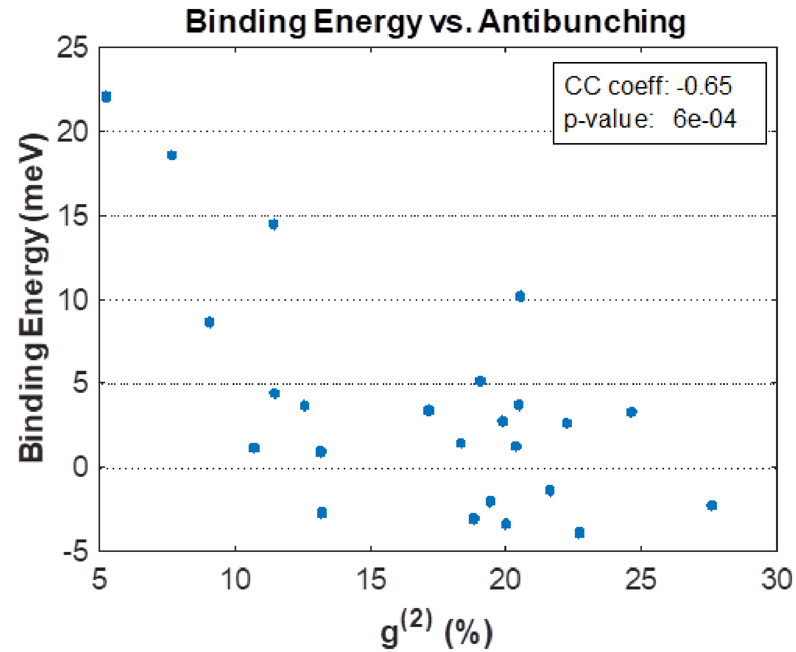


As well as correlations with other parameters (lifetime, $g^{(2)}$), providing a simple and comprehensive understanding

G. Lubin, DO, et al., ACS Nano 15, 19581 (2021)

Some hints on the role of surface chemistry





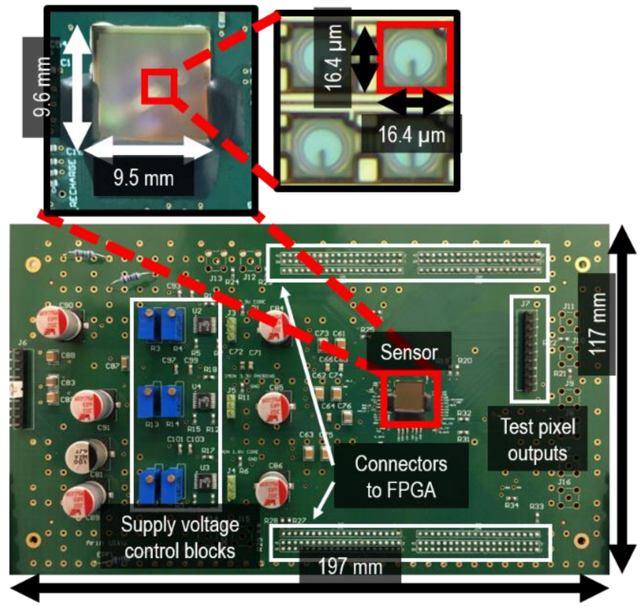
Fresh from the oven … Two different $CsPbBr_3$ samples – similar nanocrystals, different surface chemistry

Same trends, but some quantitative differences

G. Lubin, DO, et al., ACS Nano 15, 19581 (2021)

Prospects of the technique

- SPAD array technology is moving forward quickly, so heralded spectroscopy and imaging on wide fields of view are around the corner…
- Higher order processes are harder to characterize ; 3rd order is probably possible but crosstalk becomes a real barrier
- NIR SPADs are moving forward fast, possibly expanding the range of asccessible materials



Conclusions

Photon correlations are ubiquitous and are becoming not so hard to measure

They often contain information which is hard or impossible to obtain by other means

Advances in detector technology (especially CMOS-compatible SPAD arrays) will make this a simple and cheap tool to use

This is particularly interesting in the context of perovskite nanocrystals, as new information can be obtained which is hard to measure in bulk

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