Quantum Optical Spectroscopy

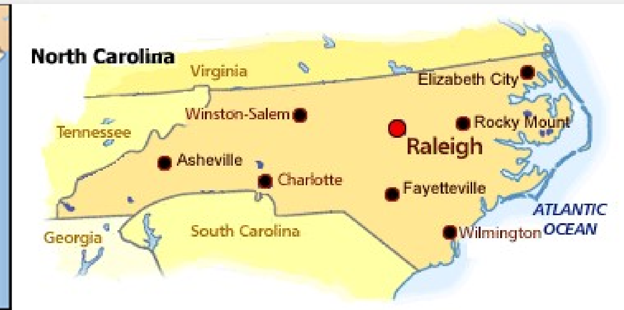
Ajay Ram Srimath Kandada

srimatar@wfu.edu

Wake Forest University

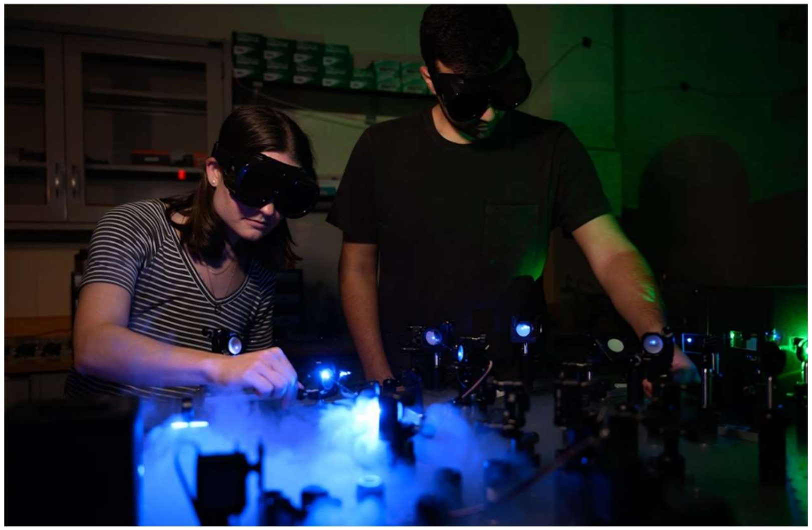
WAKE FOREST UNIVERSITY

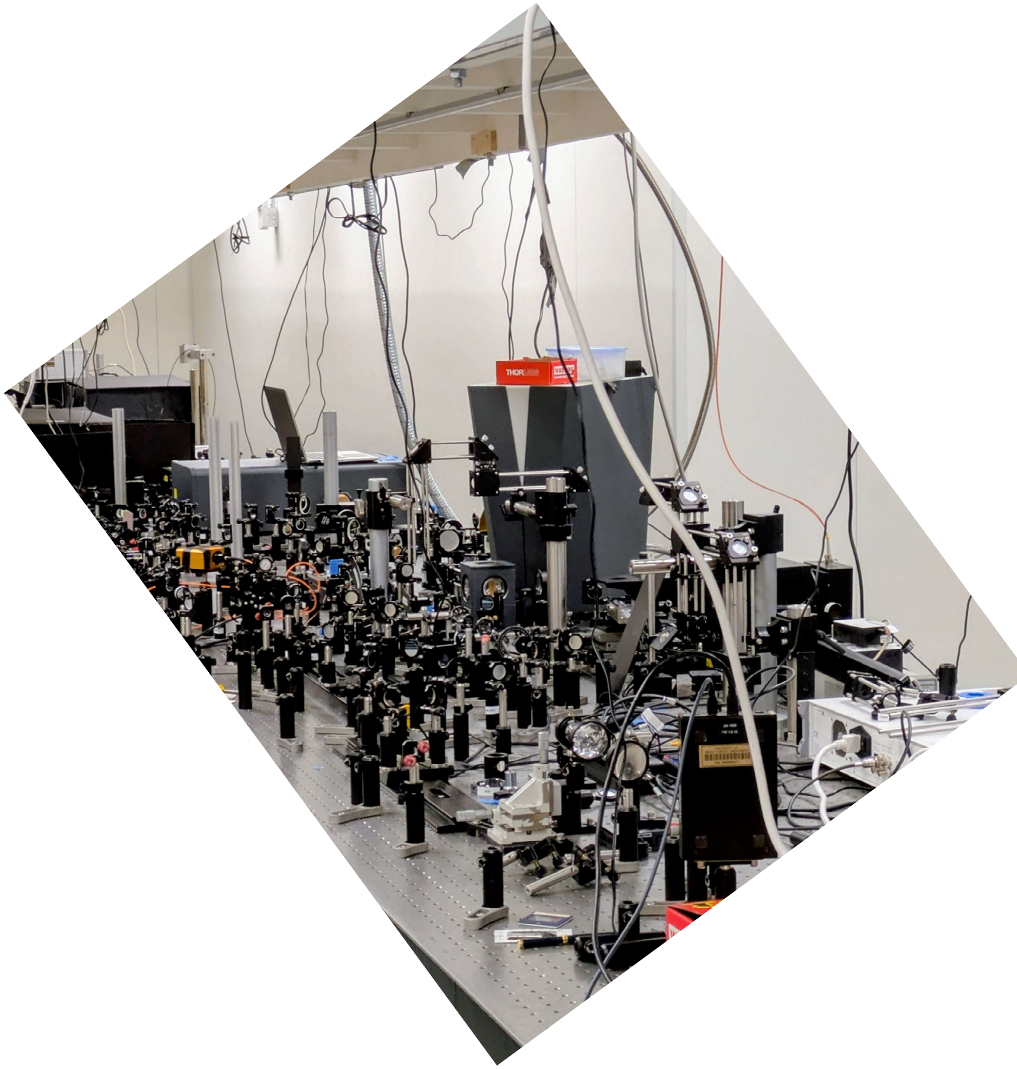
NORTH CAROLINA



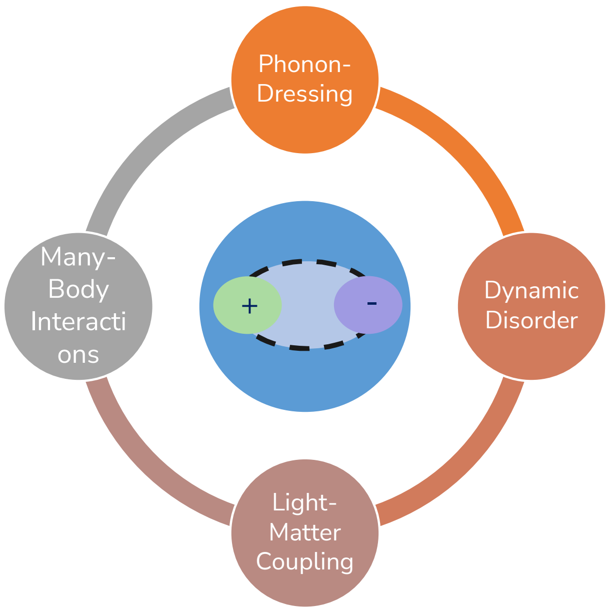
WISTON-SALEM

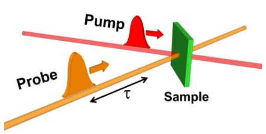
Quantum Ultrafast Optical Spectroscopy (QuantumUFOs) @ Wake Forest: 2022 - Present

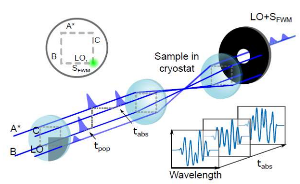


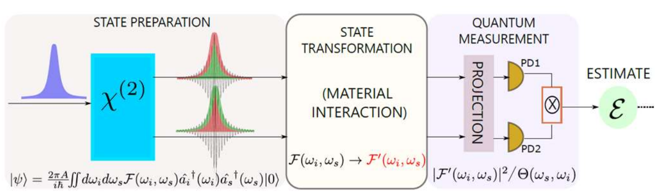


Quantum Ultrafast Optical Spectroscopy (QuantumUFOs) @ Wake Forest: 2022 - Present









Excitons in 2D Perovskites

arXiv:2503.11890
arXiv:2502.08521
JPCC 126 (12), 5378-5387
Mater Adv 4 (7), 1720-1730
JPCC 127 (43), 21194-21203

Perovskite Nanocrystals

Adv. Opt. Mater. 12 (31), 2401483
J. Chem. Phys. 160, 221101
J. Phys: Mater 7 (2), 025002
ACS nano 18 (3), 2325-2334

Strong light-matter coupling and Polariton condensates

arXiv:2404.14744
arXiv:2505.08674
ACS nano 19 (11), 10579-10588
ACS Photonics, 12, 5, 2423–2431

Quantum photons as optical probes

J. Chem. Phys. 159, 084201
arXiv:2504.14086
arXiv:2309.04751

Outline

- Classical Baseline
    - Basics of photo-detection
    - Intro to quantum mechanical description of light
- Generation of Quantum Light
    - Parametric processes – classical Vs quantum
    - SPDC – Joint Spectral Amplitude
    - SPDC – Squeezed state
- Photon Detection
    - Anatomy of detection - Photon number resolving capability
    - Intensity correlations – classification of light
    - Homodyne detection and squeezing parameter
    - Hong-Ou-Mandel Interferometry
- Paradigms for Spectroscopy
    - Sensitivity – squeezed state detection
    - Resource – JSA as a probe of correlations
    - Witness – HOM as a probe of coherence

Optical Spectroscopy – classical picture

Classical picture - Electromagnetic wave

$$P^{(1)} = \epsilon_0(\chi^{(1)} \cdot E)$$

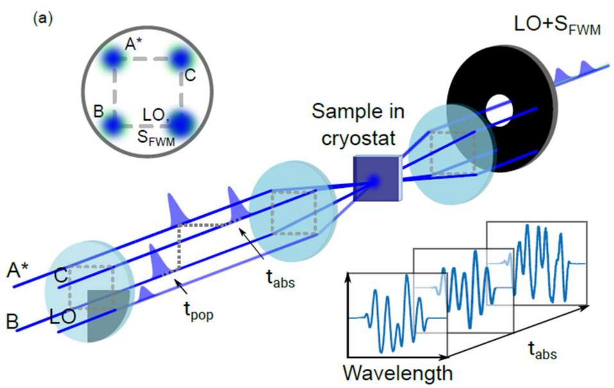
At the detector, one measures the **intensity** of the EM wave (at times, the amplitude and phase!):

$$\int_0^\infty \left|E_0(t) + E^{(1)}(t)\right|^2 dt$$

$$A\,(\omega) \propto 2\,\Re\left(P^{(1)}(\omega)\right) = 2\Re\int_0^\infty dt\; e^{i\omega t}\,\langle\mu(t)\mu(0)\rho(-\infty)\rangle$$

Absorption Spectrum

Nonlinear Spectroscopy



$$P = \epsilon_0(\chi^{(1)} \cdot E + \chi^{(2)} \cdot E \cdot E + \chi^{(3)} \cdot E \cdot E \cdot E + \cdots)$$

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 S^{(3)}(t_3, t_2, t_1) E(t - t_3) E(t - t_3 - t_2) E(t - t_3 - t_2 - t_1)$$

$$S^{(3)}(t_3, t_2, t_1) \propto \left(\frac{i}{\hbar}\right)^3 \langle \hat{\mu}(t_3 + t_2 + t_1)[\hat{\mu}(t_2 + t_1), [\hat{\mu}(t_1), \hat{\mu}(0)]]\rangle$$

- The nonlinear response in a typical three-pulse experiment is assumed to be of the third order.
- Typical intensities are very high, and multi-order responses are inevitably present
- The response is limited by the shot-noise limit

- By the nature of the experiment, the response is estimated to be a ensemble average.

- The detection scheme intrinsically lacks access to critical information regarding the statistical fluctuations that are driven either by system-bath interactions or intrinsic quantum noise.

The Central Question

Classical Spectroscopy

Question: “How much energy did the material absorb, and what are the timescales?”

Observable: Intensity (or amplitude and phase)

Limit: Shot Noise (Poissonian)

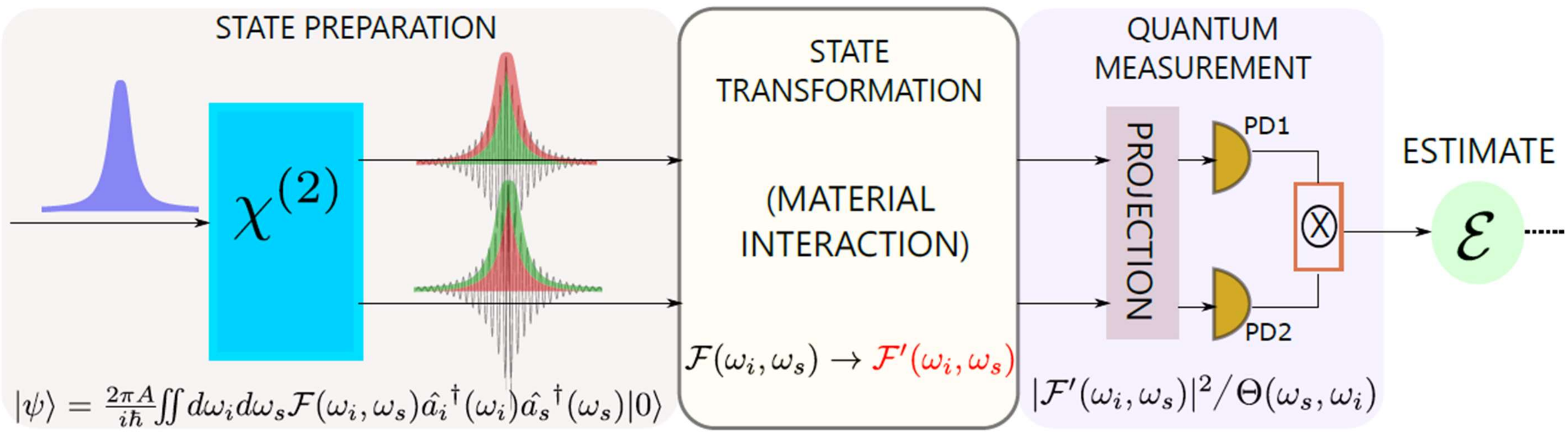
Quantum Spectroscopy

Question: “How much information did the material add to the photon’s state?”

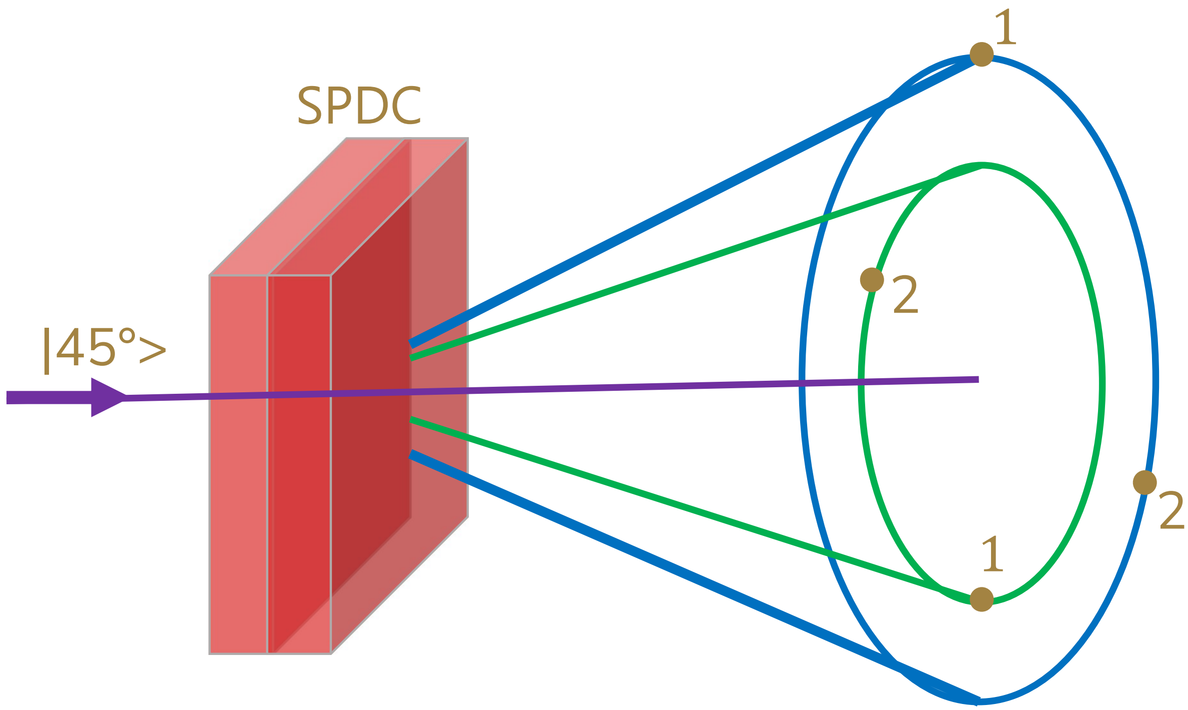
Observables: Correlation functions $g^{(2)}(\tau)$, Noise variance ΔX^2, Entanglement entropy

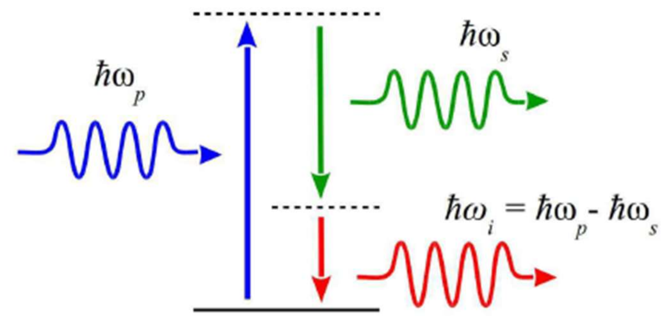
Limit: ??

Quantum Optical Spectroscopy – our perspective



Quantum state preparation – Parametric processes (NLO)





Nonlinear processes: wave equations

Maxwell's equation for a Wave propagating in a medium: $\frac{\partial^2 E}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2}$

Nonlinear Polarization: $P(z,t) = P_L(z,t) + P_{NL}(z,t)$

$$\frac{\partial^2 E}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P_L}{\partial t^2} + \mu_0 \frac{\partial^2 P_{NL}}{\partial t^2}$$

Electric Displacement: $D(z,t) = \epsilon_0 E(z,t) + P_L(z,t)$

Wave equation for nonlinear processes: $\boxed{\frac{\partial^2 E(z,t)}{\partial z^2} - \mu_0 \frac{\partial^2 D(z,t)}{\partial t^2} = \mu_0 \frac{\partial^2 P_{NL}(z,t)}{\partial t^2}}$

Let us consider just the second order processes : $P_{NL}\,(z,t) = \epsilon_0 \chi^{(2)} E^2(z,t) = 2\epsilon_0 d_{eff} E^2(z,t)$

Second order processes

Consider a EM field given by: $E(t) = A_1 \exp(-i\omega_1 t) + A_2 \exp(-i\omega_2 t) + cc$

$$E(t)^2 = (A_1 A_1^* + A_2 A_2^*)$$

$$+ A_1^2 \exp(-2i\omega_1 t)$$
$$+ A_2^2 \exp(-2i\omega_2 t)$$

$$+ 2A_1 A_2 \exp(-i(\omega_1 + \omega_2)t)$$

$$+ 2A_1 A_2^* \exp(-i(\omega_1 - \omega_2)t)$$

Optical rectification

Second harmonic generation

Sum frequency generation

Difference frequency generation

Second order processes

Considering SFG in a nonlinear crystal, the total field is given by:

$$E(z,t) = \frac{1}{2}\left\{A_1(z)\, e^{i(\omega_1 t - k_1 z)} + A_2(z)\, e^{i(\omega_2 t - k_2 z)} + A_3(z)\, e^{i(\omega_3 t - k_3 z)}\right\} + cc$$

This must satisfy the wave equation

$$\frac{\partial^2 E(z,t)}{\partial z^2} - \mu_0 \frac{\partial^2 D(z,t)}{\partial t^2} = \mu_0 \frac{\partial^2 P_{NL}(z,t)}{\partial t^2}$$

The forcing term will be (from $P_{NL}(z,t) = \epsilon_0 \chi^{(2)} E^2(z,t)$)

$$\begin{aligned}
\frac{\partial^2 P_{NL}(z,t)}{\partial t^2} = &-\epsilon_0 d_{eff} \omega_1^2 A_2^*(z) \cdot A_3(z) \cdot e^{i(\omega_1 t - (k_3 - k_2) z)} \\
&-\epsilon_0 d_{eff} \omega_2^2 A_1^*(z) \cdot A_3(z) \cdot e^{i(\omega_2 t - (k_3 - k_1) z)} \\
&-\epsilon_0 d_{eff} \omega_3^2 A_1(z) \cdot A_2(z) \cdot e^{i(\omega_3 t - (k_1 + k_2) z)}
\end{aligned}$$

Coupled nonlinear equations

Slowly varying envelope approximation: $\left|\frac{\partial^2 A}{\partial z^2}\right| \ll 2k \left|\frac{\partial A}{\partial z}\right|$ Critical!

$$\frac{\partial A_1}{\partial z} = -i\sigma_1 A_2^* A_3 \cdot e^{-i\boldsymbol{\Delta k}z}$$

$$\omega_1 + \omega_2 = \omega_3$$

$$\frac{\partial A_2}{\partial z} = -i\sigma_2 A_1^* A_3 \cdot e^{-i\boldsymbol{\Delta k}z}$$

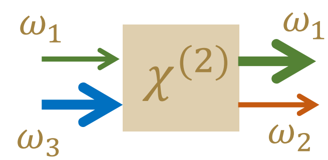
$$\sigma_i = \frac{d_{eff}\omega_i}{cn_i}$$

$$\frac{\partial A_3}{\partial z} = -i\sigma_3 A_1 A_3 \cdot e^{-i\boldsymbol{\Delta k}z}$$

$$\Delta k = k_3 - k_2 - k_1$$

Phase mismatch

DFG – relevant for parametric amplification



$$\frac{\partial A_1}{\partial z} = -i\sigma_1 A_2^* A_3 \cdot e^{-i\boldsymbol{\Delta k}z}$$

$$\frac{\partial A_2}{\partial z} = -i\sigma_2 A_1^* A_3 \cdot e^{-i\boldsymbol{\Delta k}z}$$

$$\frac{\partial A_3}{\partial z} = -i\sigma_3 A_1 A_3 \cdot e^{-i\boldsymbol{\Delta k}z}$$

Boundary conditions:

$$\frac{\partial A_3}{\partial z} = 0$$

$$A_2(z=0) = 0$$

$$\omega_1 + \omega_2 = \omega_3$$

$$\Delta k = k_3 - k_2 - k_1$$

$$I_2(z) = I_{10}\frac{\omega_2}{\omega_1}\left[\frac{\Gamma}{g}\sinh(gL)\right]^2$$

$$I_1(z) = I_{10}\left\{1 + \left[\frac{\Gamma}{g}\sinh(gz)\right]^2\right\} \cong \frac{I_{10}}{4}\left(\frac{\Gamma}{g}\right)^2 e^{2gz}$$

Highest efficiency of the amplification

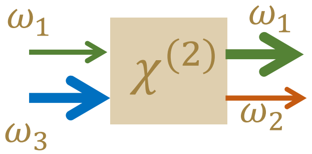
$$\Gamma^2 \approx \frac{2d_{eff}^2\omega_2\omega_3}{c^3\epsilon n_1 n_2 n_3} I_3$$

Highest g

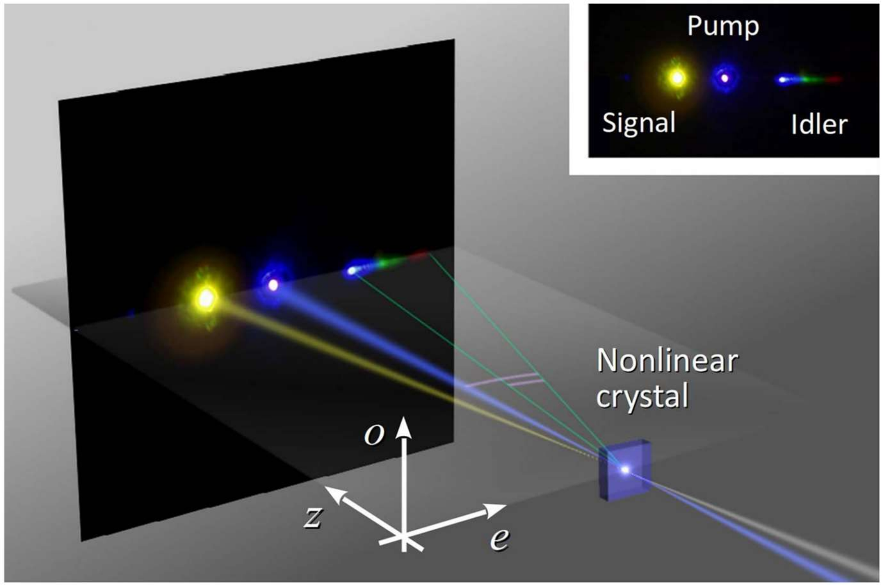
$$\boxed{\Delta k = 0}$$

$$g = \sqrt{\Gamma^2 - \frac{\Delta k^2}{4}}$$

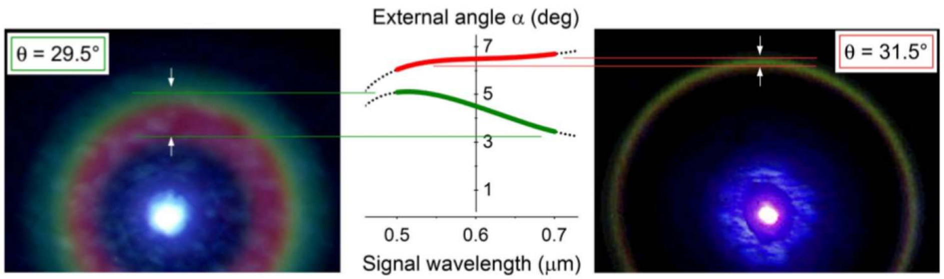
Parametric amplification



$$I_1(z) = I_{10}\left\{1 + \left[\frac{\Gamma}{g}\sinh(gz)\right]^2\right\} \cong \frac{I_{10}}{4}\left(\frac{\Gamma}{g}\right)^2 e^{2gz}$$

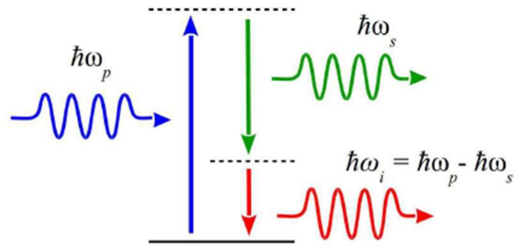


Manzoni et al



Unpublished data

SPDC – Quantum mechanical formulation



$$\hat{H}_I(t) = \epsilon_0 \int_V d^3\mathbf{r}\, \chi^{(2)} \left[\hat{E}_p^{(+)}(\mathbf{r},t)\hat{E}_o^{(-)}(\mathbf{r},t)\hat{E}_e^{(-)}(\mathbf{r},t) + h.c.\right]$$

$$\hat{E}_j^{(+)}(z,t) = \int d\omega_j \mathcal{A}(\omega_j)\hat{a}_j(\omega_j)e^{i(k_j(\omega_j)z-\omega_j t)}$$

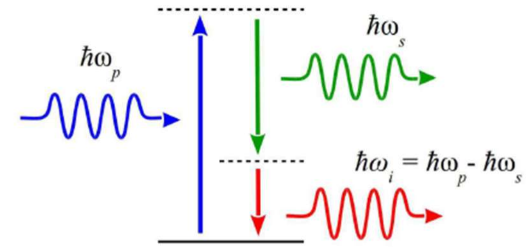
$$|\Psi(t)\rangle = \exp\left[-\tfrac{i}{\hbar}\int_{t_0}^{t} dt'\hat{H}_I(t')\right]|\Psi_0\rangle$$

Weak interaction approximation – low conversion efficiency

$$|\Psi(t)\rangle \approx \left(\mathbb{I} - \frac{i}{\hbar}\int_{-\infty}^{\infty} dt'\hat{H}_I(t')\right)|vac\rangle$$

$$\text{Term} \propto \int_{-\infty}^{\infty} dt' \int_{-L/2}^{L/2} dz \iiint d\omega_p d\omega_o d\omega_e\, \alpha(\omega_p)\, \hat{a}_o^{\dagger}(\omega_o)\hat{a}_e^{\dagger}(\omega_e)$$
$$\times \exp\left(-i\{[k_o + k_e - k_p]z - [\omega_o + \omega_e - \omega_p]t'\}\right)$$

SPDC – Quantum mechanical formulation



$$\int_{-\infty}^{\infty} dt'\, e^{i(\omega_p-\omega_o-\omega_e)t'} = 2\pi\delta(\omega_p-\omega_o-\omega_e)$$

Energy conservation

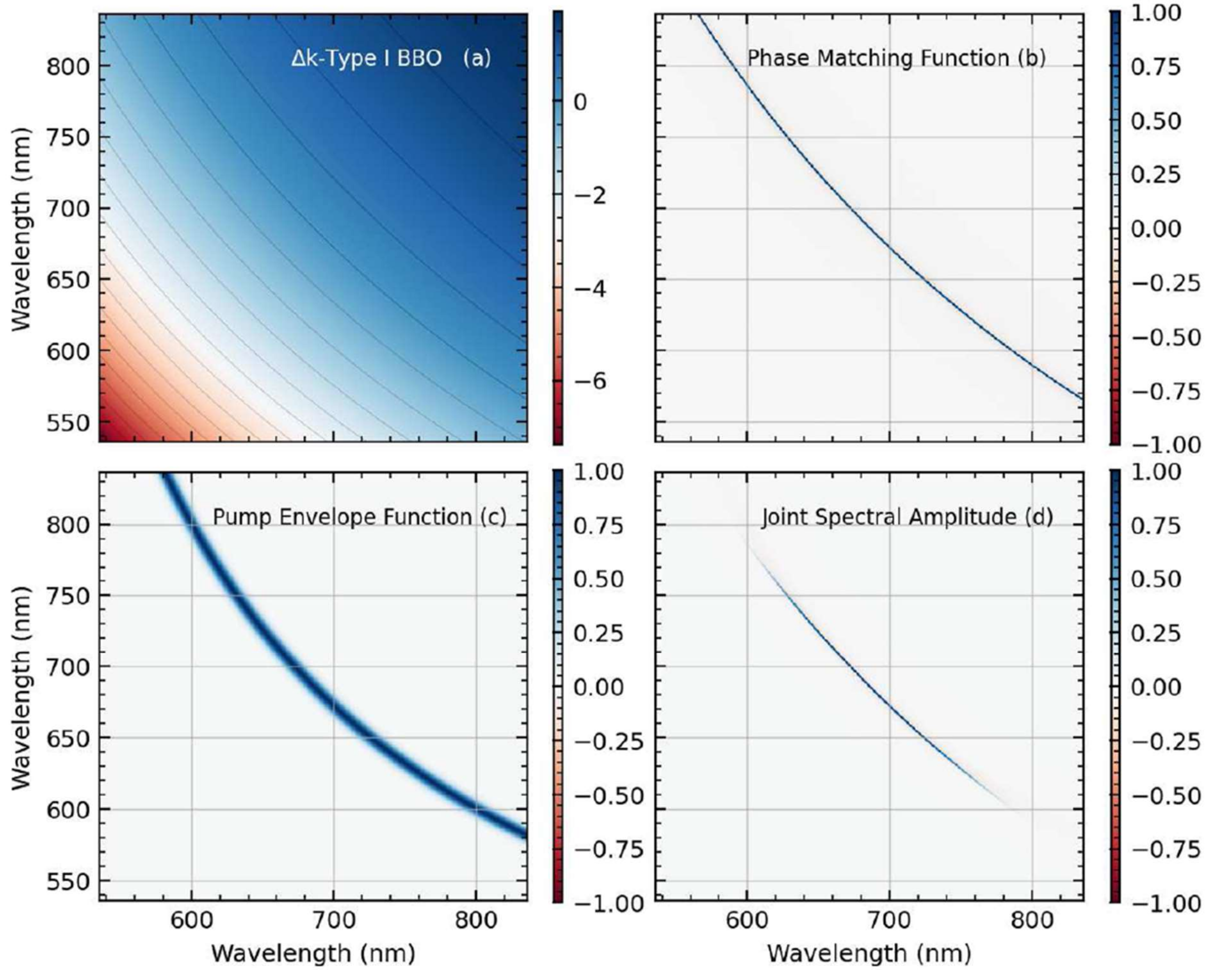
$$\int_{-L/2}^{L/2} dz\, e^{-i(k_o+k_e-k_p)z} = L\,\mathrm{sinc}\left(\frac{\Delta k L}{2}\right)$$

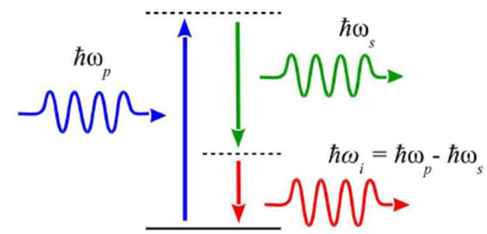
Momentum conservation/
Phase-matching function

$$|\Psi\rangle_{\mathrm{SPDC}} = |vac\rangle + C\iint d\omega_o d\omega_e \;\underbrace{\alpha(\omega_o+\omega_e)}_{\text{Pump Envelope}}\;\underbrace{\Phi(\Delta k)}_{\text{Phase Matching}}\;\hat{a}_o^\dagger(\omega_o)\hat{a}_e^\dagger(\omega_e)|vac\rangle$$

$$f(\omega_o,\omega_e) = \alpha(\omega_o+\omega_e)\times\Phi(\Delta k)$$ Joint Spectral Amplitude

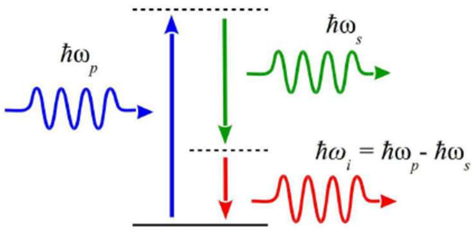
$$|\psi\rangle = \frac{2\pi A}{i\hbar} \int\int d\omega_i d\omega_s \mathscr{F}(\omega_i, \omega_s)\hat{a}_i^{\dagger}(\omega_i)\hat{a}_s^{\dagger}(\omega_s)|0\rangle$$





J. Chem. Phys. 159, 084201

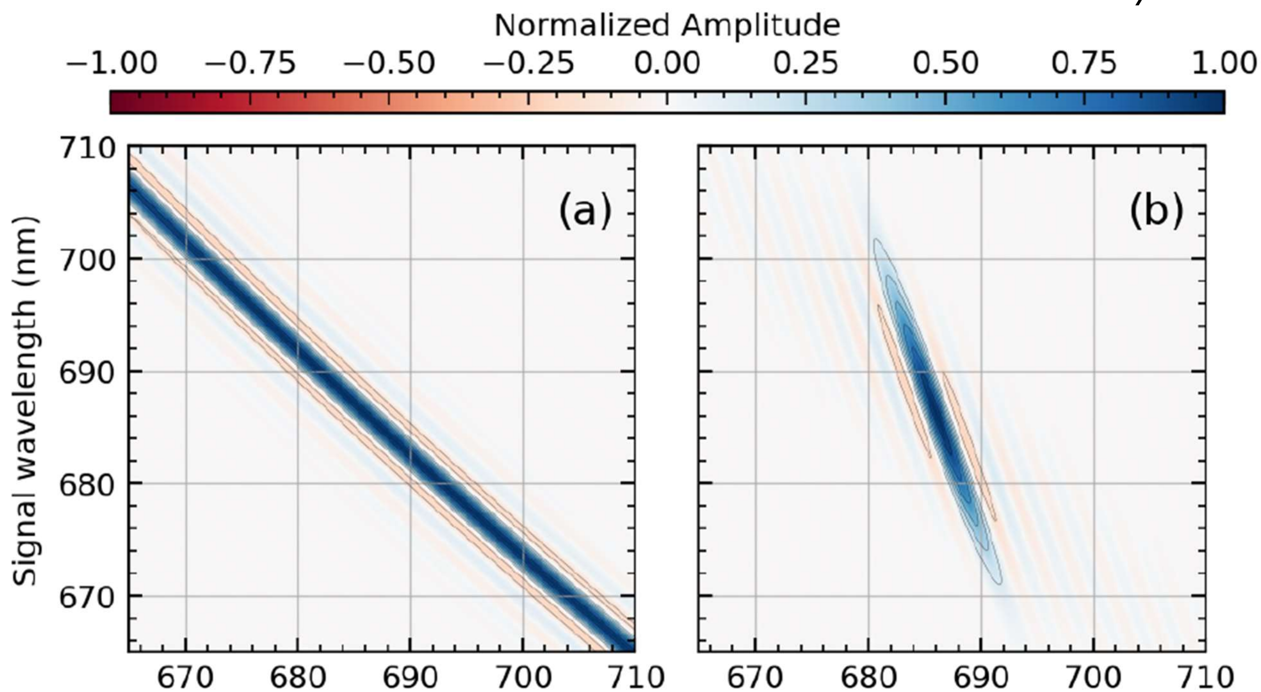
SPDC in Type I and Type II BBO crystals



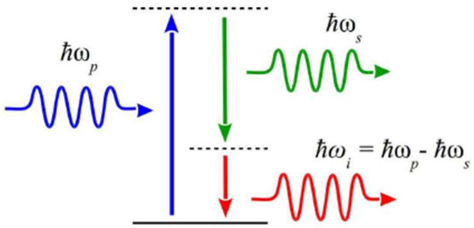
$$|\psi\rangle = \frac{2\pi A}{i\hbar} \int\int d\omega_i d\omega_s \mathscr{F}(\omega_i, \omega_s) \hat{a}_i^{\dagger}(\omega_i) \hat{a}_s^{\dagger}(\omega_s) |0\rangle$$

J. Chem. Phys. 159, 084201

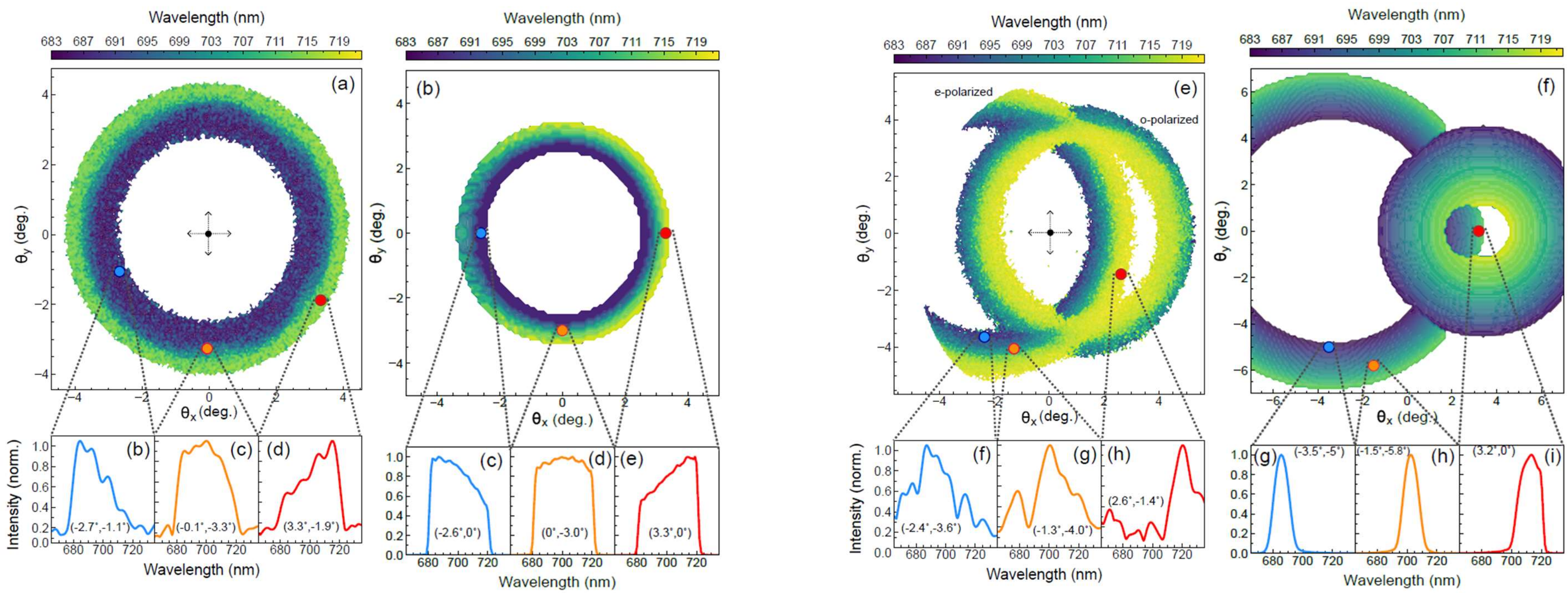
Joint Spectral Amplitude (JSA)



SPDC in Type I and Type II BBO crystals - spectrally filtered



$$|\psi\rangle = \frac{2\pi A}{i\hbar}\int\int d\omega_i d\omega_s \mathscr{F}(\omega_i,\omega_s)\hat{a}_i^{\dagger}(\omega_i)\hat{a}_s^{\dagger}(\omega_s)|0\rangle$$



Kumar et al Optica Open (2025)

Quantum mechanical treatment of light

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{q}^2$$

$$[\hat{q}, \hat{p}] = i\hbar$$

Quadrature operators

$$\hat{X}_1 = \frac{\hat{q}}{\sqrt{\hbar/2\omega m}} = \frac{1}{2}[\hat{a}^\dagger + \hat{a}]$$

$$\hat{X}_2 = \frac{\hat{p}}{\sqrt{\hbar\omega m/2}} = \frac{i}{2}[\hat{a}^\dagger - \hat{a}]$$

Heisenberg uncertainty

$$\Delta X_1 \Delta X_2 \geq \frac{1}{4}$$

$$\hat{H} = \frac{\hbar\omega}{4}\left(\hat{X}_1{}^2 + \hat{X}_2{}^2\right)$$

$$= \hbar\omega\left(\hat{a}^\dagger\,\hat{a} + \frac{1}{2}\right)$$

$$\hat{N} = \hat{a}^\dagger\,\hat{a}$$

$$\hat{N}\,|n\rangle = n\,|n\rangle$$

Number operator

$$\equiv \textit{infinite Hilbert space with basis} \rightarrow |\boldsymbol{n}\rangle \rightarrow \boldsymbol{\textit{Fock or number state}}$$

Quantum mechanical treatment of light

$$\hat{H} = \frac{\hbar\omega}{4}\left({\hat{X}_1}^2 + {\hat{X}_2}^2\right)$$

$$= \hbar\omega\left(\hat{a}^\dagger\,\hat{a} + \frac{1}{2}\right)$$

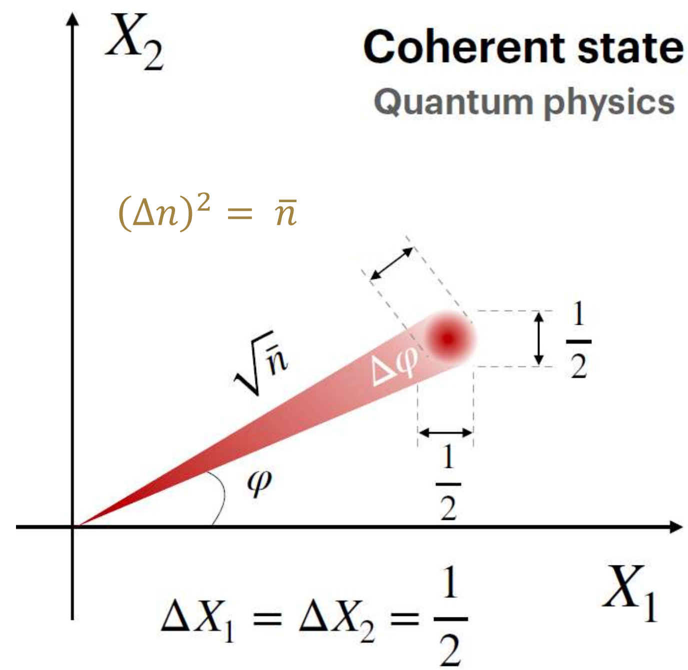
Number operator

$$\hat{N} = \hat{a}^\dagger\,\hat{a}$$

$$\hat{N}\,|n\rangle = n\,|n\rangle$$

Number of photons in the mode

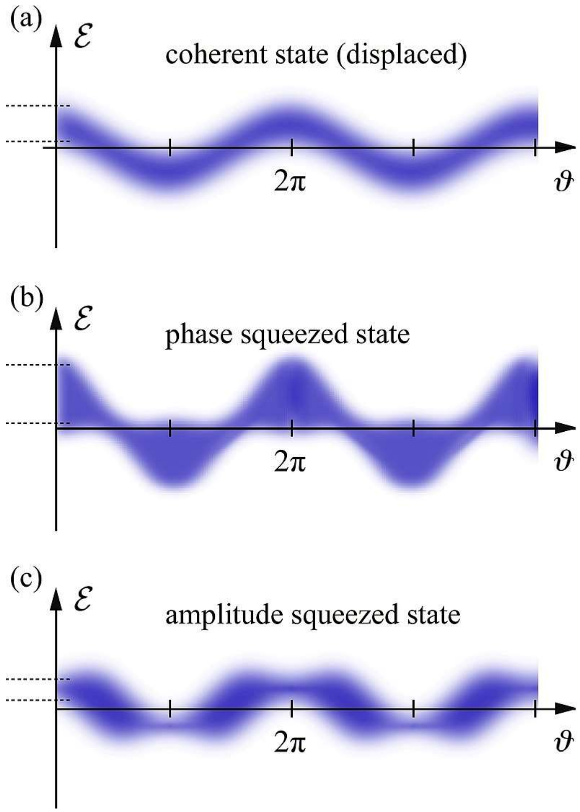
Phase space trajectory



Coherent state (classical): $\Delta X_1 = \Delta X_2 = 0$

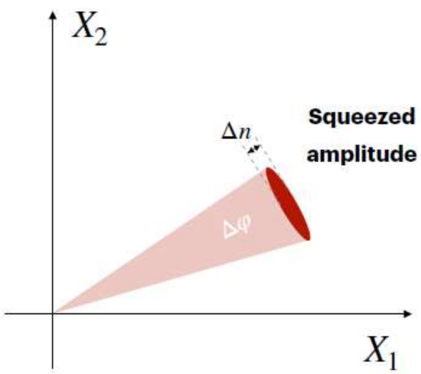
Coherent state (quantum): $\Delta X_1 = \Delta X_2$ =1/2

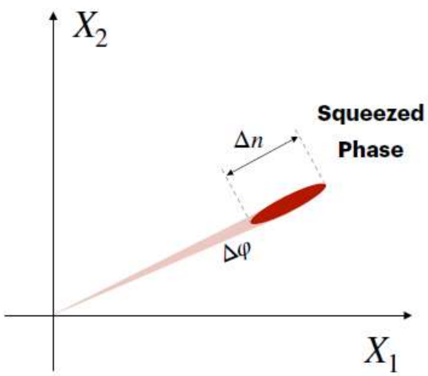
Squeezed states of light



$$\hat{S}(\xi) = e^{\frac{1}{2}\left(\xi^* \hat{a}^2 - \xi \hat{a}^{\dagger 2}\right)}$$

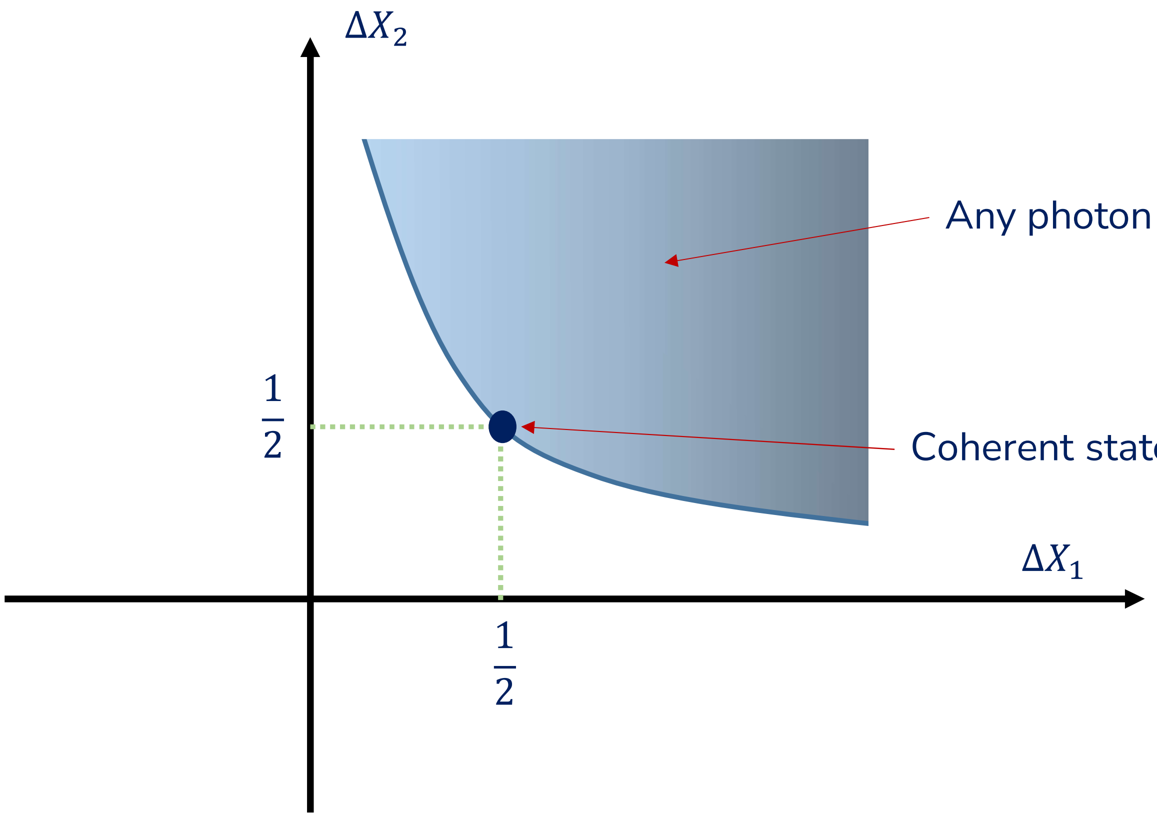
$$\xi = re^{i\theta}$$





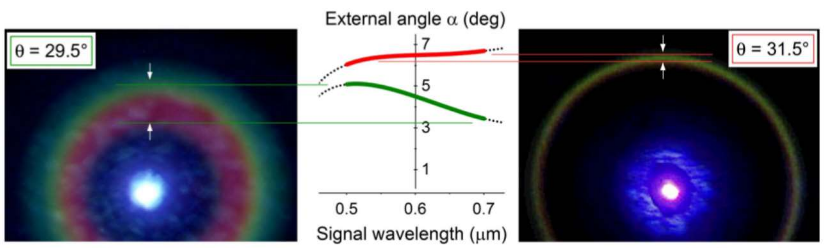
$$\hat{S}^\dagger(\xi)\hat{a}\hat{S}(\xi) = \hat{a}\cosh r - \hat{a}^\dagger e^{i\theta}\sinh r$$

Squeezed states of light



One can increase precision on one of the quadratures, by sacrificing the other – Squeezed light!

Squeezed states of light – SPDC as a source



$$\hat{H}_{SPDC} \propto i\hbar\chi^{(2)}(\hat{a}_p\hat{a}_s^\dagger\hat{a}_i^\dagger - h.c.)$$

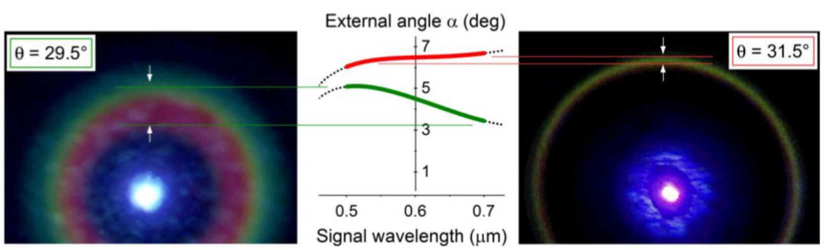
$$\hat{a}^\dagger\hat{a}^\dagger = (\hat{a}^\dagger)^2$$

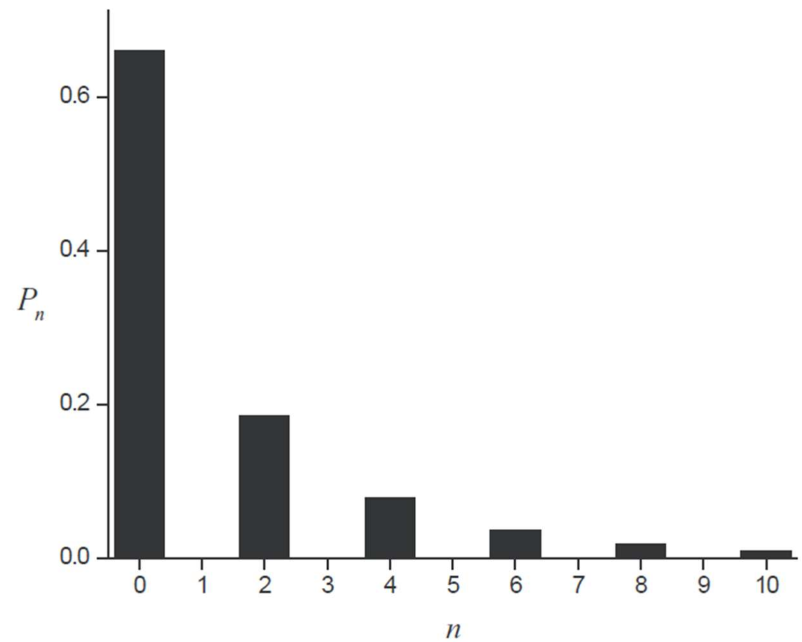
$$\hat{H}_{deg} = \frac{i\hbar\eta}{2}((\hat{a}^\dagger)^2 - \hat{a}^2) \quad \eta \propto \chi^{(2)}\beta$$

$$\hat{S}(\xi) = e^{\frac{1}{2}\left(\xi^* \hat{a}^2 - \xi \hat{a}^{\dagger 2}\right)}$$

$$\hat{U}(t) = \exp\left[\frac{\eta t}{2}((\hat{a}^\dagger)^2 - \hat{a}^2)\right]$$

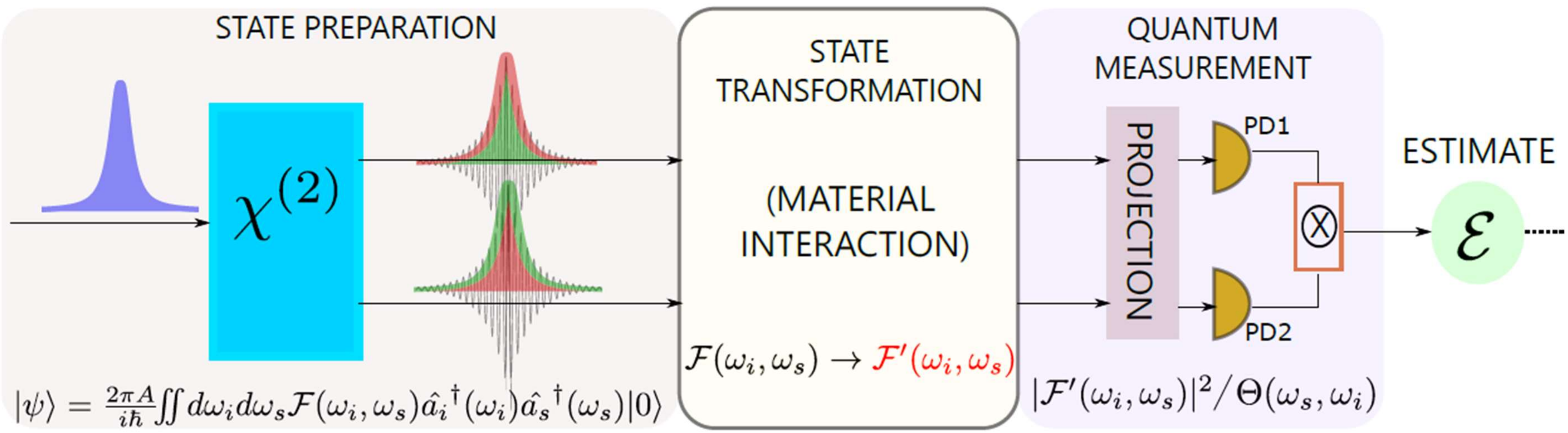
Squeezed states of light – SPDC as a source





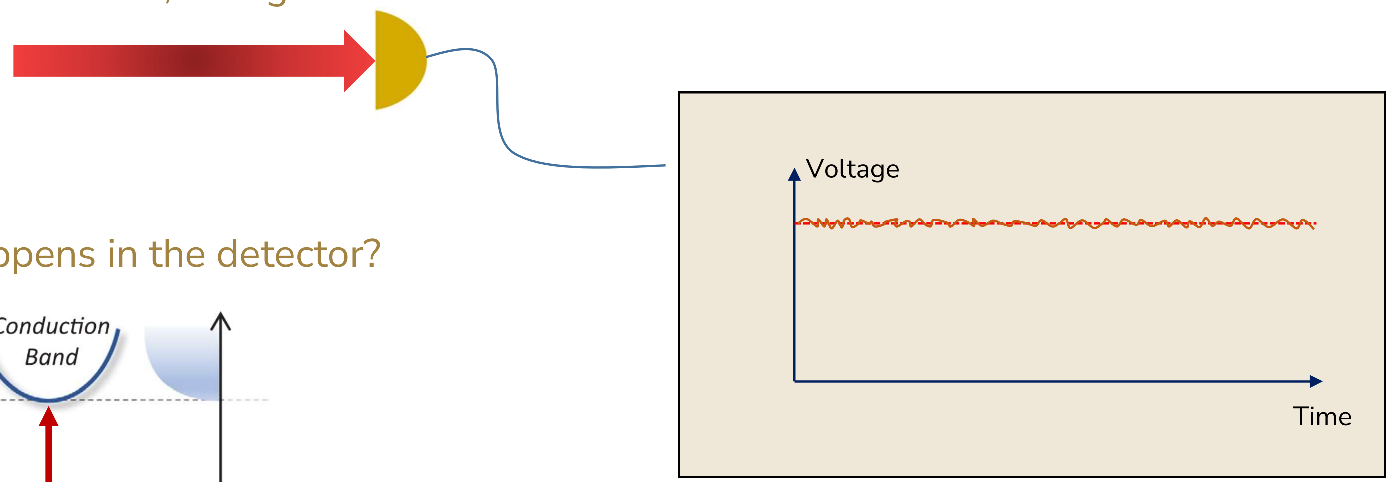
$$\hat{S}(\xi) = e^{\frac{1}{2}\left(\xi^* \, \hat{a}^2 - \xi \, \hat{a}^{\dagger 2}\right)}$$

Quantum Optical Spectroscopy – our perspective

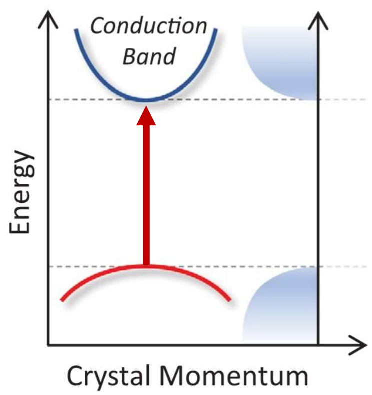


Detecting an EM wave

Monochromatic, cw light



What happens in the detector?

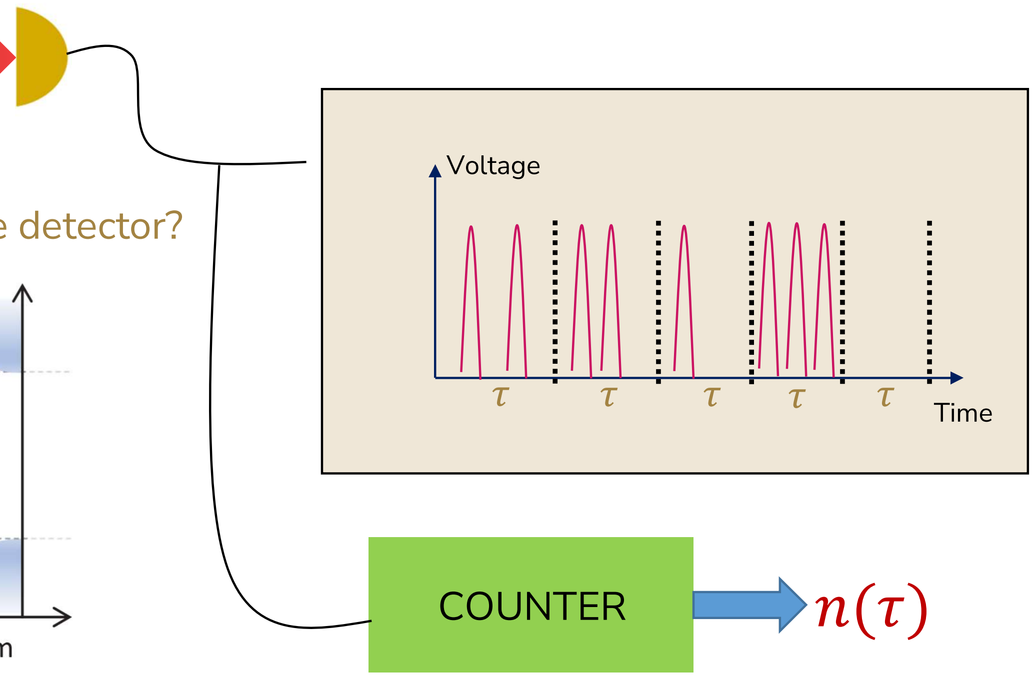


$$i(t) = \frac{D'}{t} \int_0^t I(t')dt'$$

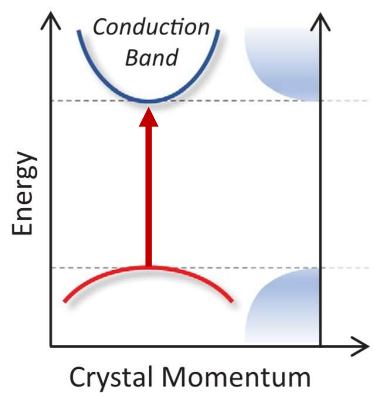
Detection is intrinsically stochastic!

Detecting an EM wave

Monochromatic, cw light



What happens in the detector?



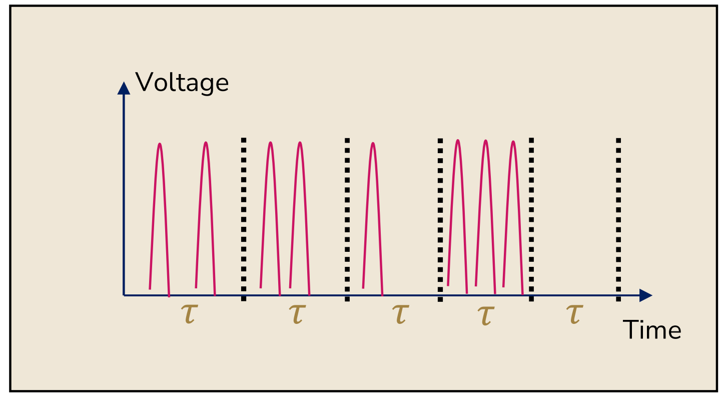
Detection is intrinsically stochastic!

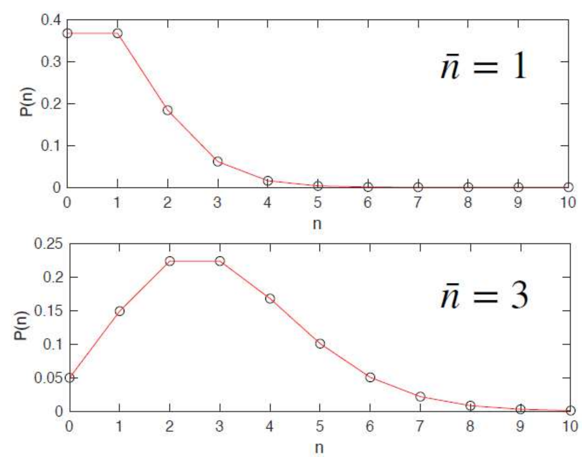
Statistics of photodetection

COUNTER $\rightarrow n(\tau)$

$\bar{n}$ Mean

$(\Delta n)^2$ Variance





Poisson distribution

$$P\,(n) = \frac{\bar{n}^n}{n!} e^{-\bar{n}}$$

$$\bar{n} \;= (\Delta n)^2$$

Classification of light based on statistics

Statistics	Classification		Examples
$\bar{n} < (\Delta n)^2$	Super Poissonian	Intensity I = I(t)	Thermal light Partially coherent light
$\bar{n} = (\Delta n)^2$	Poissonian	Intensity constant	Coherent light
$\bar{n} > (\Delta n)^2$	Sub-Poissonian	Intensity constant	QUANTUM LIGHT

Glauber's theory of detection

- Detectors function by absorbing photons – Interaction:

$$\hat{H}_{int} \propto \hat{\mu} \cdot \hat{E}$$

- Transition rate

$$w(t) \propto \sum_f |\langle f|\hat{E}^{(+)}|i\rangle|^2 = \langle i|\hat{E}^{(-)}\hat{E}^{(+)}|i\rangle$$

Normal Ordering

The rate is proportional to $\langle \hat{a}^\dagger \hat{a}\rangle$. For the Vacuum state $|0\rangle$:

$$\hat{a}|0\rangle = 0 \implies w(t) = 0$$

Physical detectors do not "click" due to vacuum fluctuations.

Anatomy of detection

$$\eta_{det} = \eta_{coupling} \times \eta_{abs} \times \eta_{elec}$$

Discrimination threshold to avoid dark noise

Optical coupling

Internal quantum efficiency
Generation of electron-hole pairs

Linear Detectors:
- Photodiodes that operate under reverse bias below the breakdown voltage.
- No internal gain– used for bright light detection.
- The photocurrent is directly proportional to the instantaneous intensity.

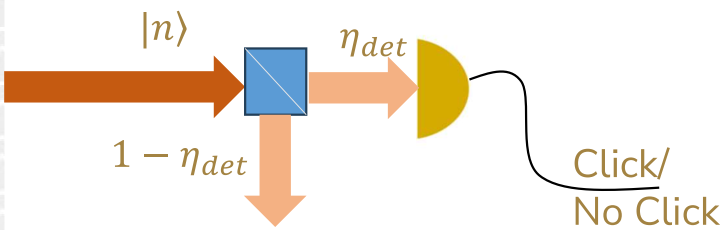
Single Photon Avalanche Diodes (SPADs)
- Impact Ionization – gain of 10^5-10^6
- Output – A macroscopic voltage spike (a TTL pulse)
  The size of the avalanche is determined by the bias voltage, and not by the number of photons.
- SPADs effectively digitize the field into “Vacuum” or “Light” – not number resolving.

Why are SPADs not photon number resolving?

Methodology – evaluate the POVMs $\{\widehat{\Pi}_k\}$

Operators that describe the probabilities of experimental outcomes

$$P\ (k) = Tr\ [\hat{\rho}\widehat{\Pi}_k]$$



$$P(\text{No Click}|n) = \underbrace{(1-\eta)\times(1-\eta)\times\cdots\times(1-\eta)}_{n\text{ times}} = (1-\eta)^n$$

$$\hat{\Pi}_0 = \sum_{n=0}^{\infty}(1-\eta)^n|n\rangle\langle n|$$

$$\hat{\Pi}_{click} = \mathbb{I} - \hat{\Pi}_0 = \sum_{n=1}^{\infty}[1-(1-\eta)^n]|n\rangle\langle n|$$

Weighted sum of ALL number states

- A "Click" does not project the state onto $|1\rangle$.
- Projects onto the subspace of "not vacuum"

Photon-number resolving detectors

Conditional Probability

$$P(n|m) = \binom{m}{n} \eta^n (1-\eta)^{m-n}$$

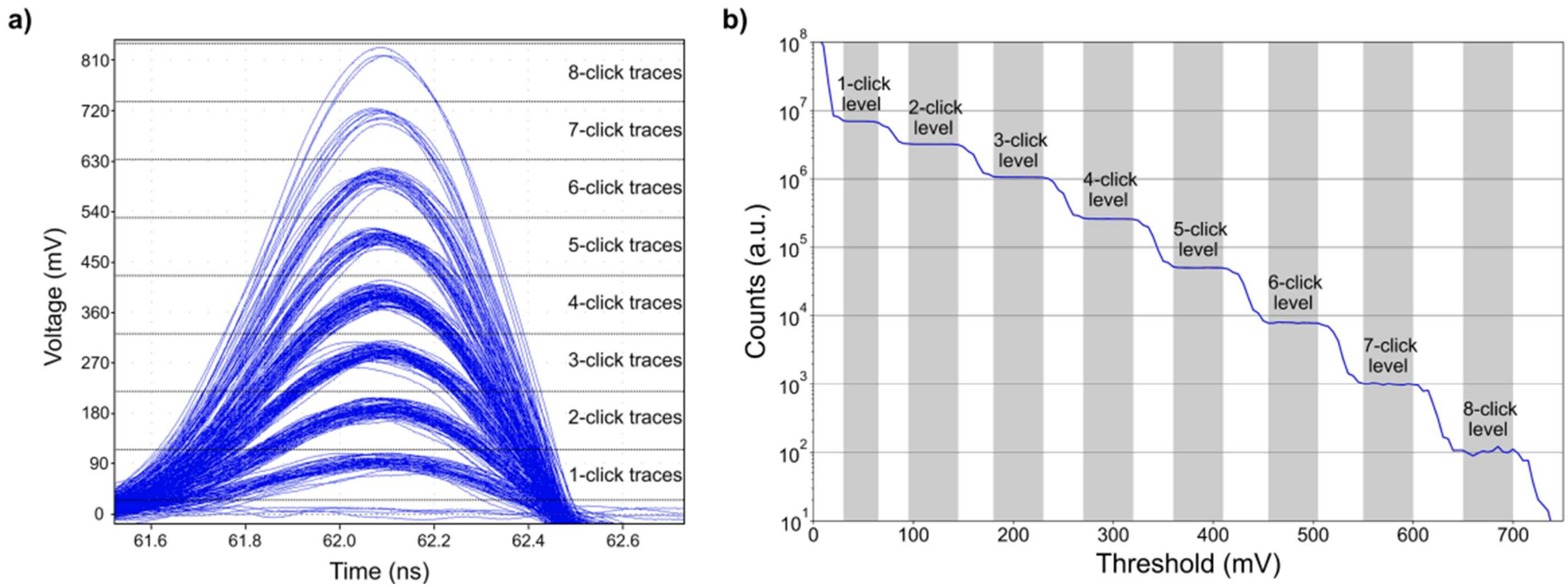
POVM

$$\hat{\Pi}_n(\eta) = \sum_{m=n}^{\infty} \binom{m}{n} \eta^n (1-\eta)^{m-n} |m\rangle\langle m|$$

- Diagonal in number basis
- In the ideal limit of $\eta \to 1$, the term vanishes unless $m = n$

$$\hat{\Pi}_n(1) = |n\rangle\langle n|$$

Photon-number resolving detectors

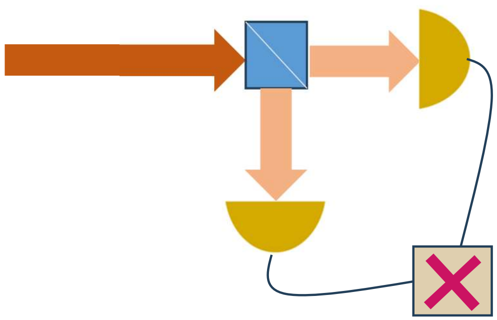


arXiv: 2406.15312

Photon-number resolving detectors

Feature	Standard SNSPD	PNR SNSPD (Array)	Transition Edge Sensor (TES)
Output	Binary (Click/No Click)	Discrete Steps (0, 1, 2... N)	Continuous Energy Reading
Speed (Jitter)	Excellent (~10 ps)	Good (~20-50 ps)	Slow (Low resolution)
Mechanism	Phase Transition (Hotspot)	Multiplexed Hotspots	Calorimetric (Heat measure)
Use Case	HBT, QKD, Timing	Boson Sampling, Non-Gaussian States	High-fidelity Number Counting

HBT setup



$$\hat{\Pi}_{coinc} = \hat{\Pi}^{(1)}_{click} \otimes \hat{\Pi}^{(2)}_{click}$$

$$\hat{\Pi}_{click} = \mathbb{I} - \sum_{n=0}^{\infty} (1-\eta)^n |n\rangle\langle n|$$

$$(1-\eta)^n \approx 1 - n\eta + \mathcal{O}(\eta^2)$$

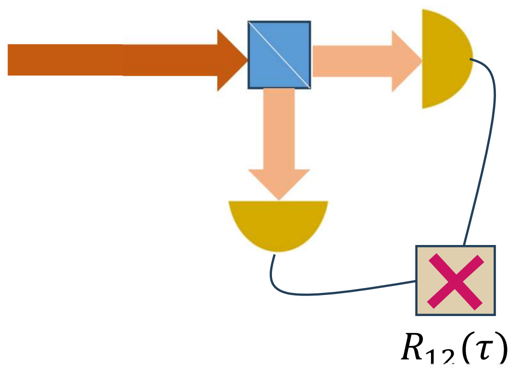
$$\hat{\Pi}_{click} \approx \sum_{n=0}^{\infty} [1-(1-n\eta)]|n\rangle\langle n| = \eta \sum_{n=0}^{\infty} n|n\rangle\langle n| = \eta\hat{n}$$

$$g^{(2)}(\tau) = \frac{\langle \hat{a}^\dagger(t)\hat{a}^\dagger(t+\tau)\hat{a}(t+\tau)\hat{a}(t)\rangle}{\langle \hat{a}^\dagger(t)\hat{a}(t)\rangle^2}$$

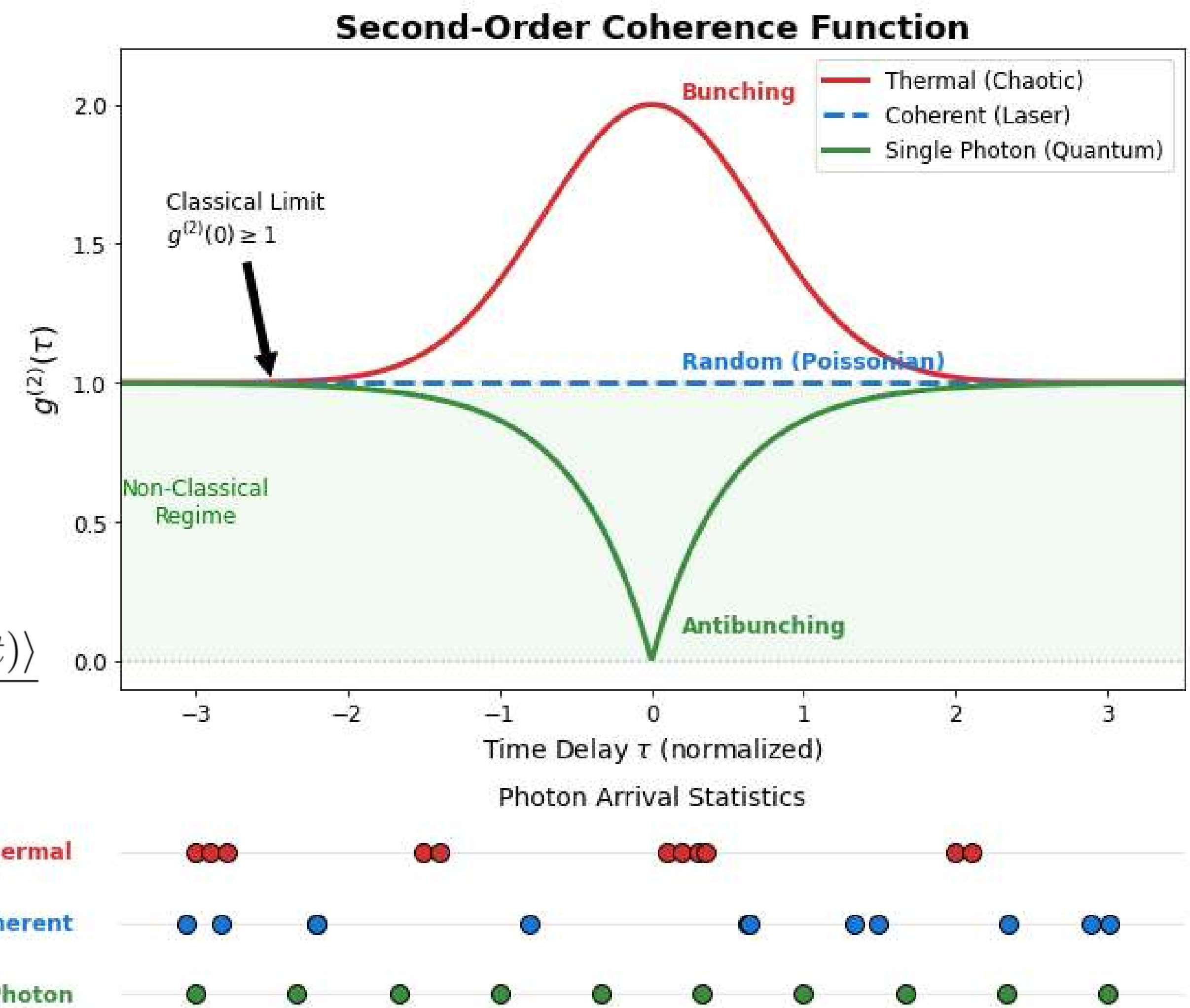
$$R_{12} \propto \langle \hat{\Pi}^{(1)}_{click}\hat{\Pi}^{(2)}_{click}\rangle \approx \eta^2 \langle \hat{n}_1\hat{n}_2\rangle$$

$$\langle : \hat{n}_1\hat{n}_2 : \rangle \propto \langle \hat{a}^\dagger\hat{a}^\dagger\hat{a}\hat{a}\rangle$$

HBT setup



$$g^{(2)}(\tau) = \frac{\langle \hat{a}^\dagger(t)\hat{a}^\dagger(t+\tau)\hat{a}(t+\tau)\hat{a}(t)\rangle}{\langle \hat{a}^\dagger(t)\hat{a}(t)\rangle^2}$$

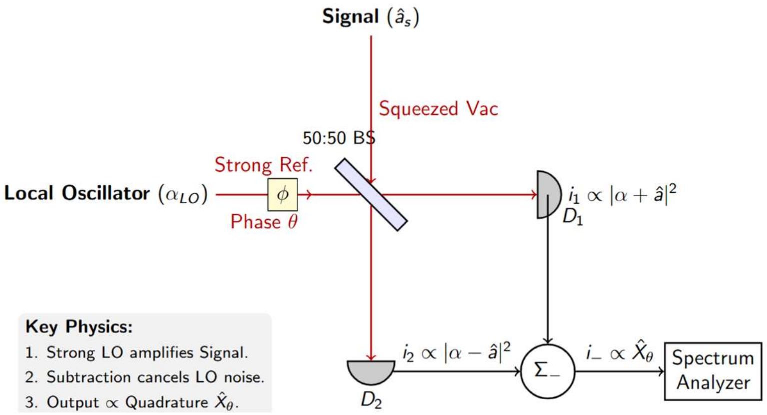


Exercises

- What is g(2) of a two-photon Fock state, estimated from a HBT setup?

- In determining g(2) of a biphoton state, if you had PNR detectors, would you still need a HBT?

Squeezed state detection



$$\hat{a}_1 = \frac{1}{\sqrt{2}}(\hat{a}_s + \hat{a}_{LO})$$

$$\hat{a}_2 = \frac{1}{\sqrt{2}}(\hat{a}_s - \hat{a}_{LO})$$

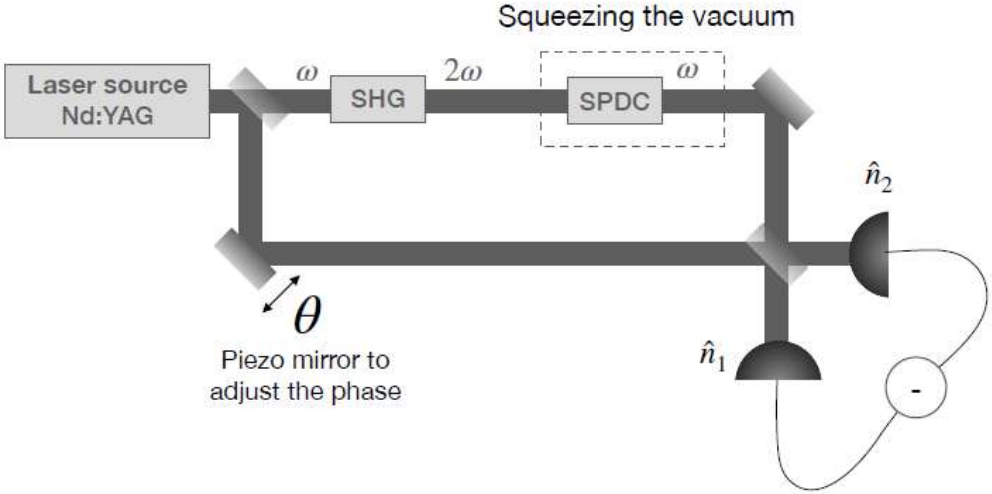
$$\hat{I}_- \propto \hat{n}_1 - \hat{n}_2 = \hat{a}_1^\dagger \hat{a}_1 - \hat{a}_2^\dagger \hat{a}_2$$

$$\hat{I}_- \propto \frac{1}{2}[(\hat{a}_s^\dagger + \alpha_{LO}^*)(\hat{a}_s + \alpha_{LO}) - (\hat{a}_s^\dagger - \alpha_{LO}^*)(\hat{a}_s - \alpha_{LO})]$$

$$\hat{I}_- \propto \alpha_{LO}^* \hat{a}_s + \alpha_{LO} \hat{a}_s^\dagger \qquad \alpha_{LO} = |\alpha| e^{-i\theta}$$

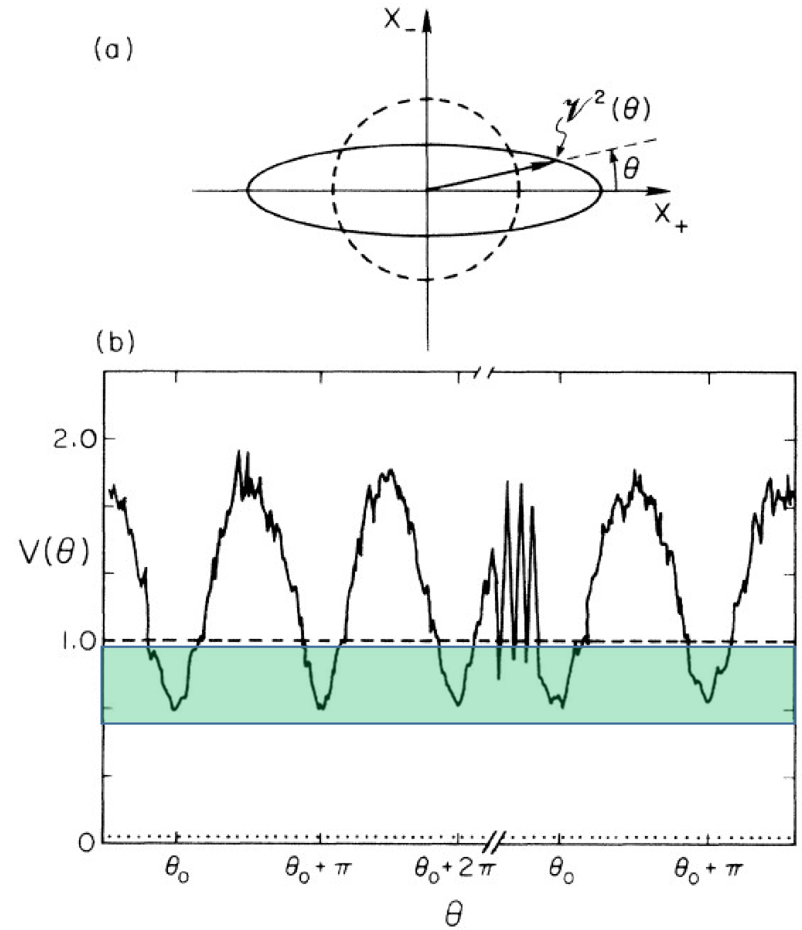
$$\hat{I}_- \propto |\alpha|(\hat{a}_s e^{-i\theta} + \hat{a}_s^\dagger e^{i\theta}) = 2|\alpha|\hat{X}_\theta$$

Squeezed light from SPDC



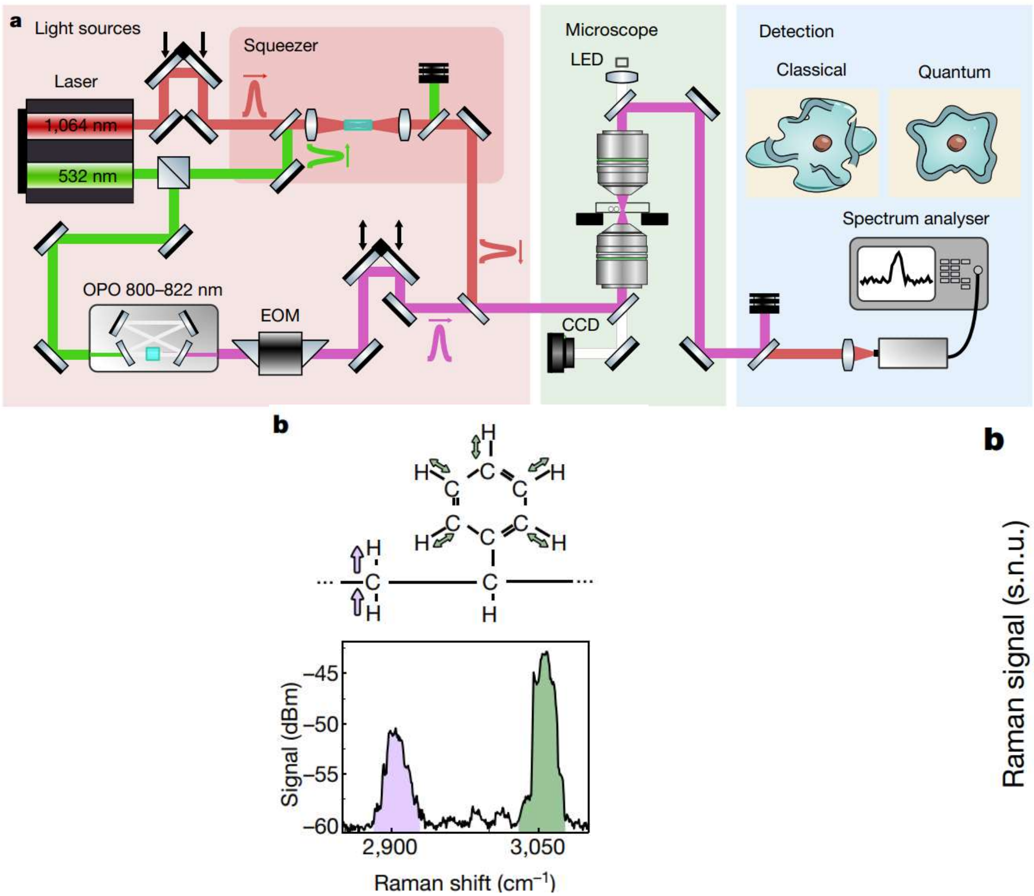
$$\hat{I}_{-} \propto |\alpha|(\hat{a}_s e^{-i\theta} + \hat{a}_s^{\dagger} e^{i\theta}) = 2|\alpha|\hat{X}_{\theta}$$

$$V(\theta) = \langle(\Delta\hat{X}_{\theta})^2\rangle = \langle\hat{X}_{\theta}^2\rangle - \langle\hat{X}_{\theta}\rangle^2$$

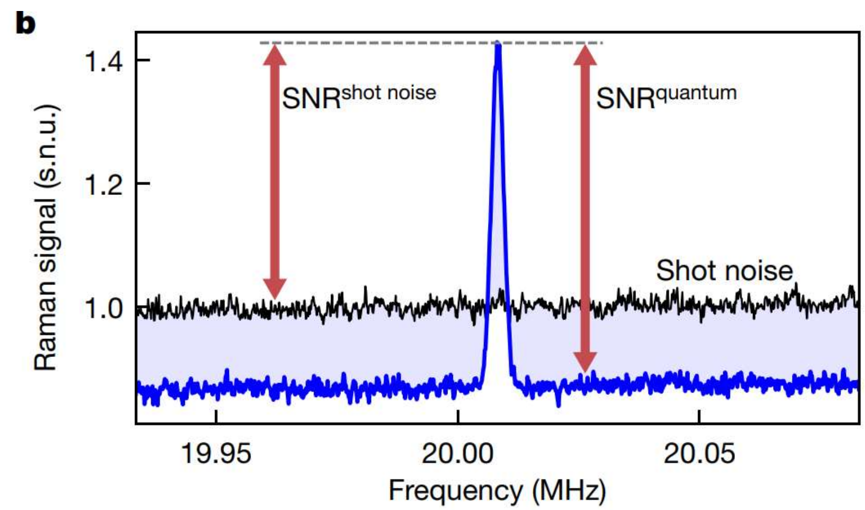


Wu et al, PRL, 57, 1986.

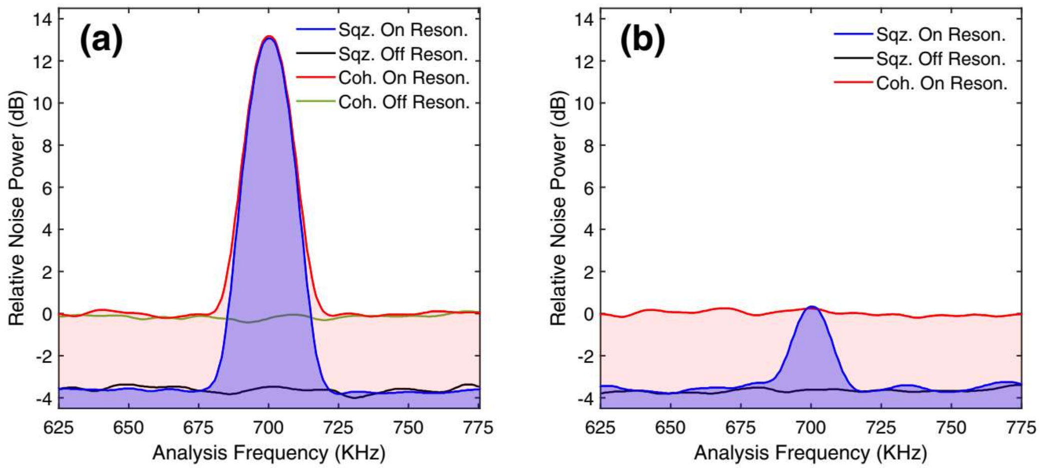
Quantum enhanced Raman spectroscopy



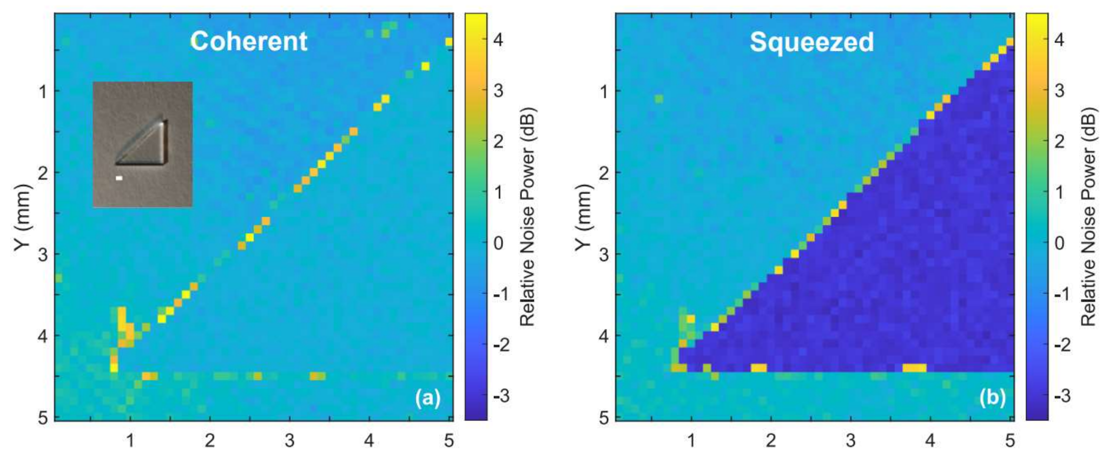
NATURE, 594, 201 (2021)



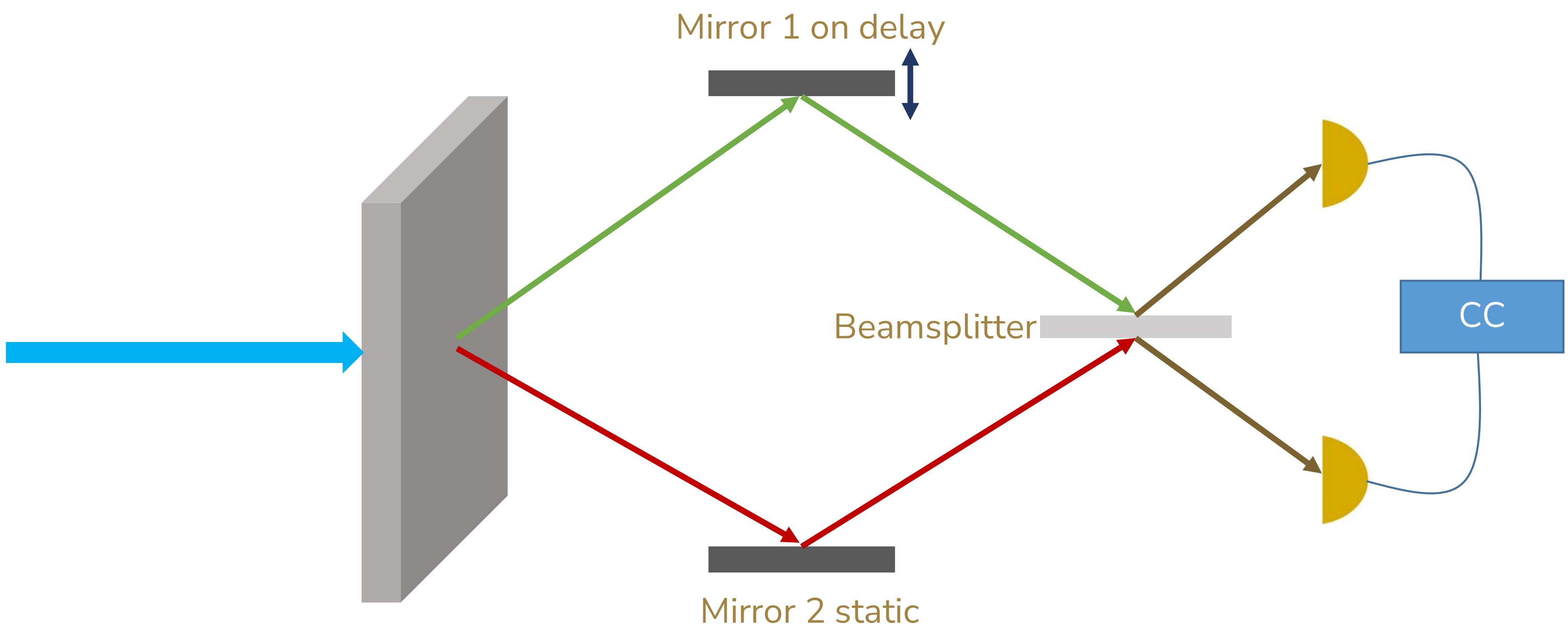
Quantum enhanced Brillouin scattering



Optica, 9, 959 (2022)

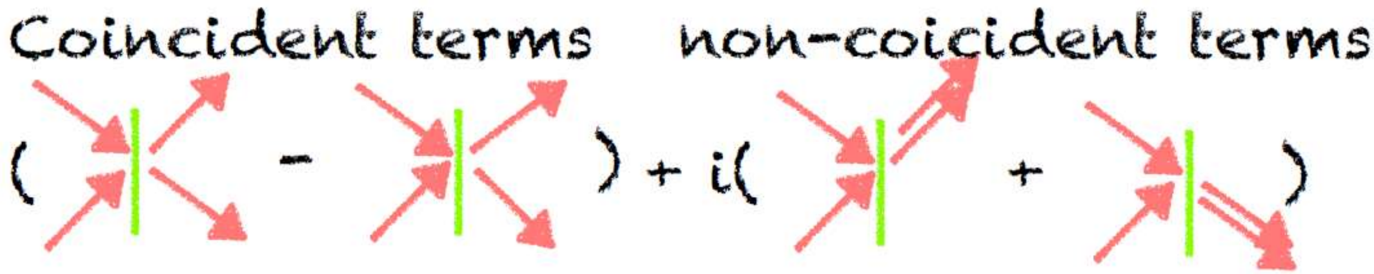


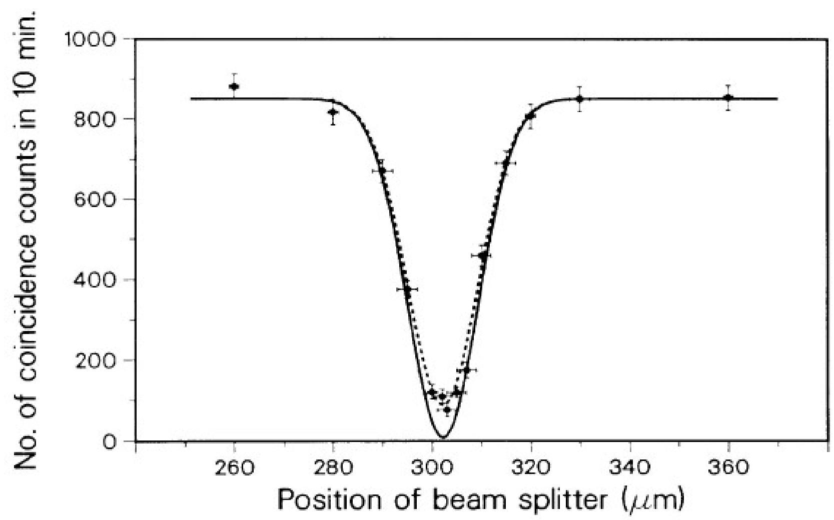
Hong-Ou-Mandel Interferometer



Hong-Ou-Mandel Interferometer

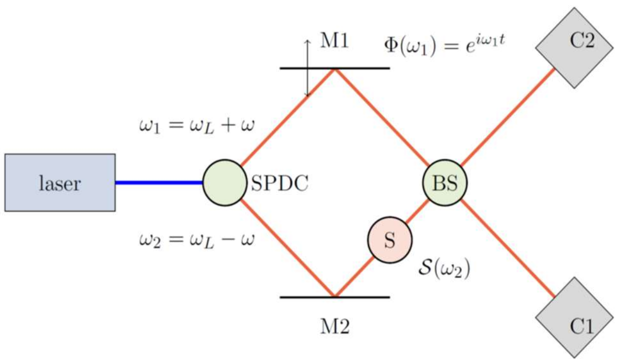
At the beamsplitter, if the photons are indistinguishable:



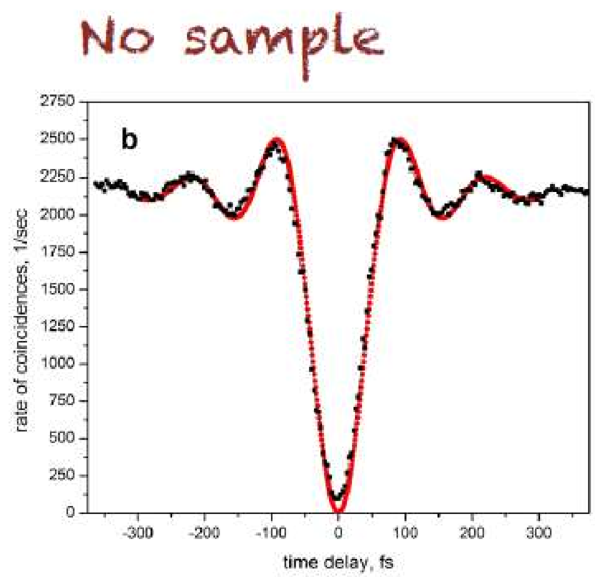


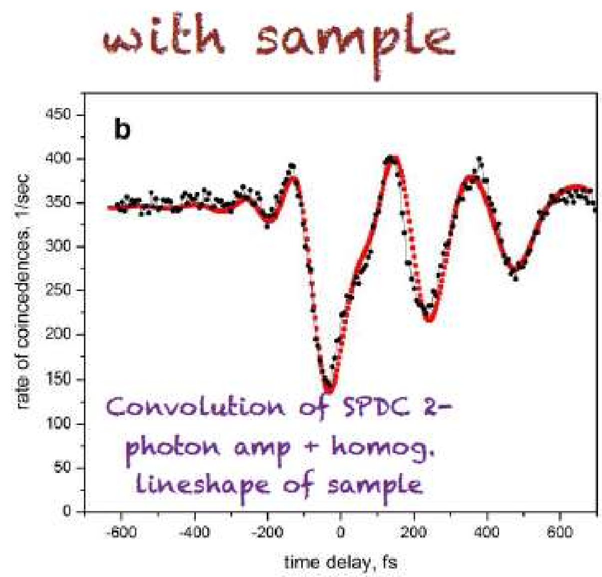
Hong et al, PRL, 59, 2044 (1987)

HOM interferometer for spectroscopy



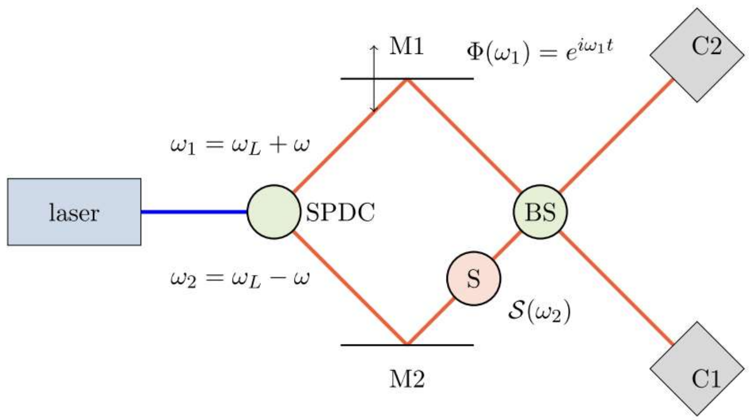
Kalashnikov et al, Scientific Reports, 7, 11444 (2017)

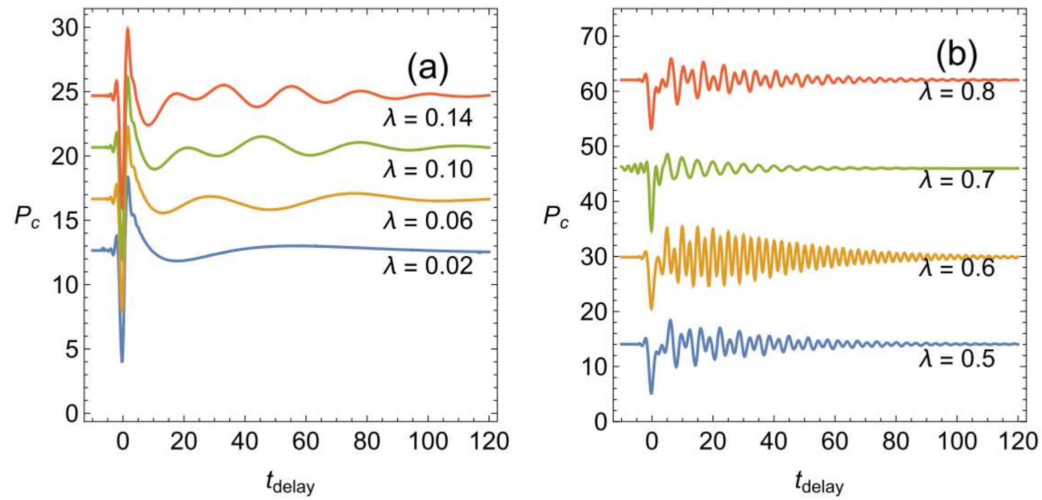




HOM INTERFEROMETRY FOR LINEAR RESPONSE

Quantum.Sci.Tech., 3, 015003



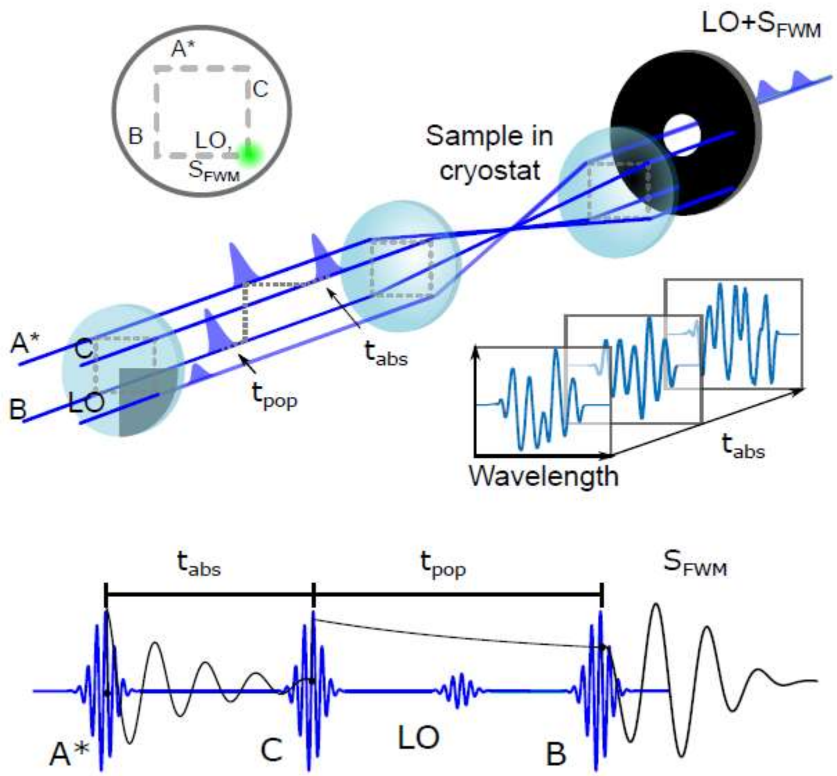


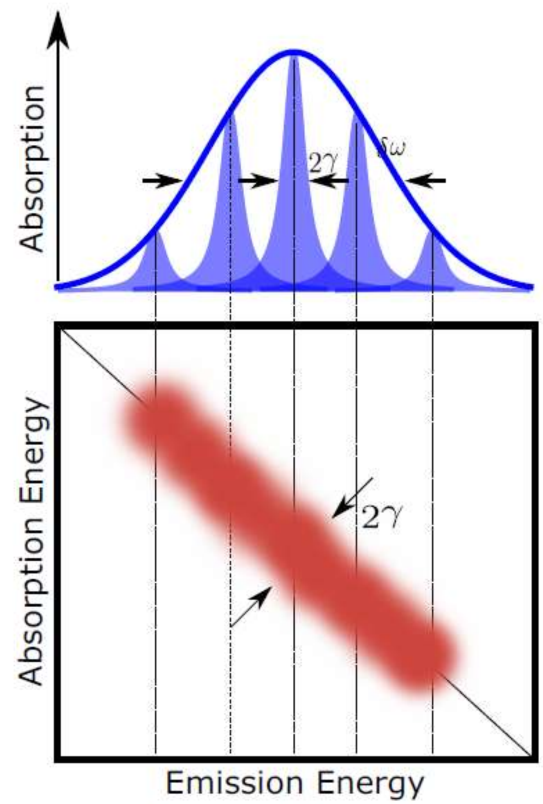
"CW" experiment with sub 100 fs dynamics

$$P_c(t_{\text{delay}}) = \frac{1}{4}\int_{-\infty}^{+\infty} \mathrm{d}z |\mathcal{F}(z)|^2 \{ |\mathcal{S}(\omega_L - z)|^2 + |\mathcal{S}(\omega_L + z)|^2 - 2\,\mathrm{Re}\,[\mathcal{S}^*(\omega_L - z)\mathcal{S}(\omega_L + z)\mathrm{e}^{-2izt_{\text{delay}}}]\},$$

- The interaction with the material preserves the initial entanglement between the two photons.
- The sample on the entanglement introduces an additional phase lag to one of the photons that can be formally introduced in the form for a scattering response function.

HOMOGENOUS LINEWIDTH FROM 2D SPECTROSCOPY

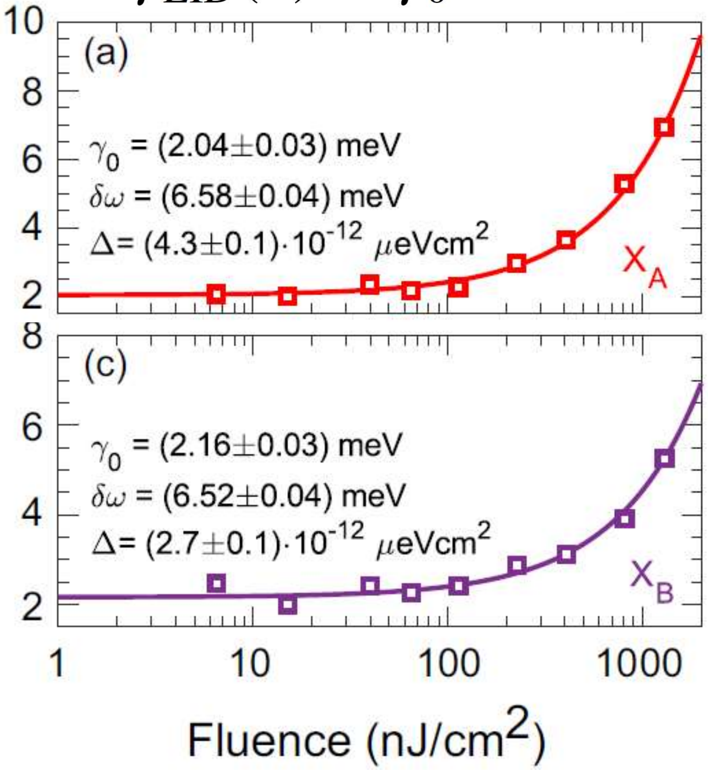


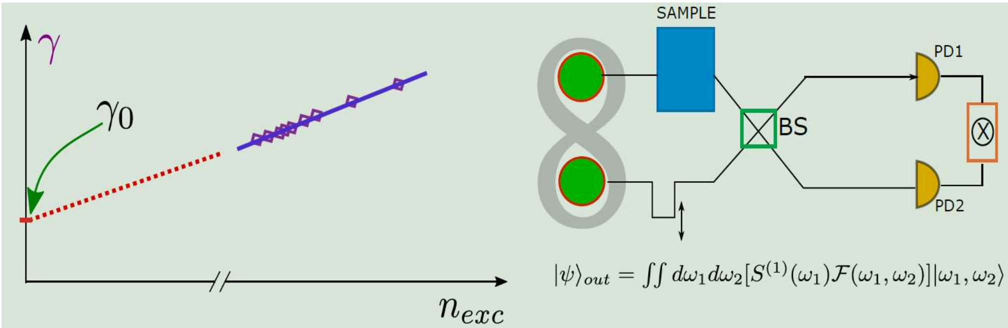


Kandada, Li, Bittner, Silva, J.Phys. Chem. C (2022)

EXCITATION INDUCED DEPHASING (EID)

$$\gamma_{\mathrm{EID}}(n) = \gamma_0 + \Delta n.$$





Can one measure the intrinsic dephasing rate with quantum light?

Thouin..Kandada, Silva, Phys. Rev. Research (2019). Kandada et al, J. Chem. Phys. (2020)

Quantum mechanical treatment of light

- Light is an electromagnetic wave, must satisfy the Maxwell equations

$$\bar{\nabla} \cdot \bar{\boldsymbol{E}} = \frac{\rho}{\epsilon_0} \qquad \bar{\nabla} \times \bar{E} = -\frac{\partial \bar{B}}{\partial t}$$

$$\bar{\nabla} \cdot \bar{\boldsymbol{B}} = 0 \qquad \bar{\nabla} \times \bar{B} = \epsilon_0 \mu_0 \frac{\partial \bar{E}}{\partial t} + \mu_0 \bar{J}$$

$$\xrightarrow{\rho = 0\ ;\ \bar{J} = 0}$$

$$\bar{B} = \bar{\nabla} \times \bar{A}$$

$$\bar{E} = -\bar{\nabla}\phi - \frac{\partial \bar{A}}{\partial t}$$

$$\left(c^2 \nabla^2 - \frac{\partial^2}{\partial^2 t}\right) \bar{\boldsymbol{A}} = \boldsymbol{0}$$

$$\bar{A}\,(z,t) = e_k \sum_k N_k q_k(t) e^{ikz}$$

Modes of an EM wave behave as harmonic oscillators!

$$H_{EM} = \sum_{n=1}^{\infty} \left(\frac{p_n^2}{2m} + \frac{m^2 \omega^2}{2} q_n \right) = \frac{1}{2} \int d^3 r \left[\epsilon_0 E^2(z,t) + \frac{1}{\mu_0} B^2(z,t) \right]$$

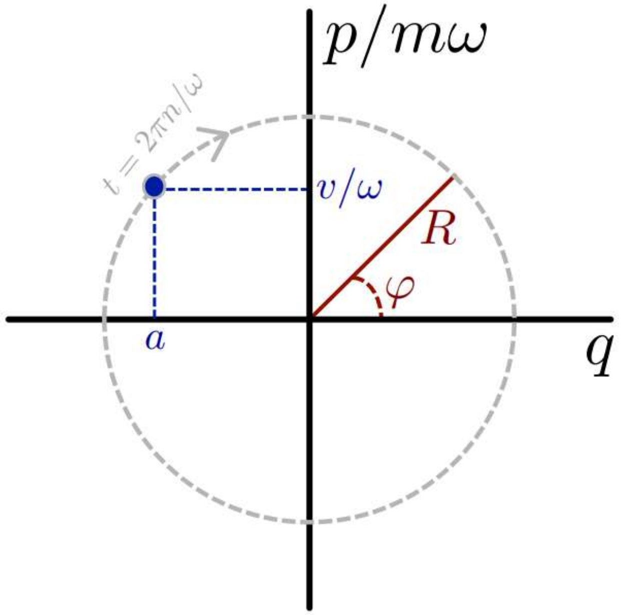
Let us look at classical harmonic oscillators

$$H_0 = \frac{p^2}{2m} + \frac{m\omega^2}{2} q^2$$

$$\dot{q} = \frac{p}{m};$$

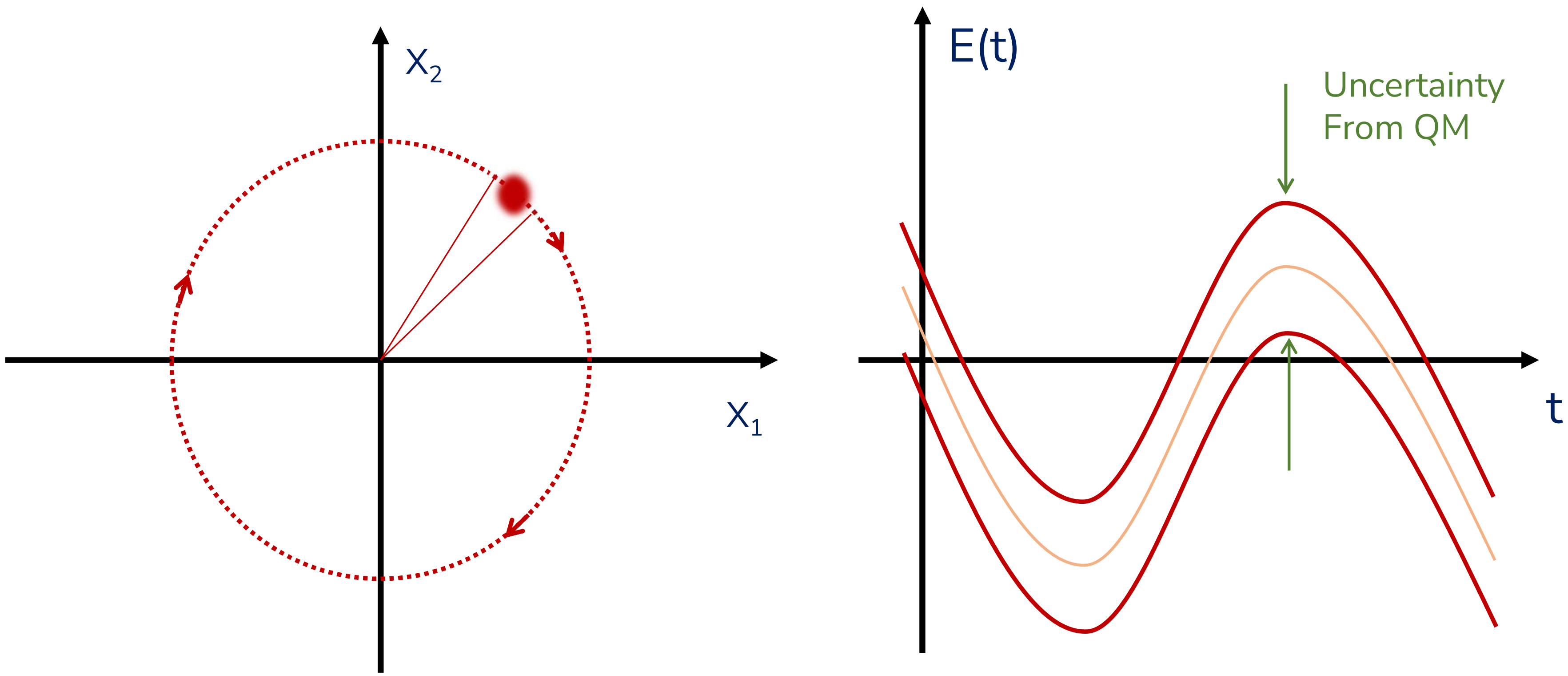
$$\dot{p} = -m\omega^2 q;$$

$$\left(q, \frac{p}{m\omega}\right) = (a \cos \omega t + \frac{v}{\omega} \sin \omega t \,, \frac{v}{\omega} \cos \omega t \; - a \sin \omega t$$



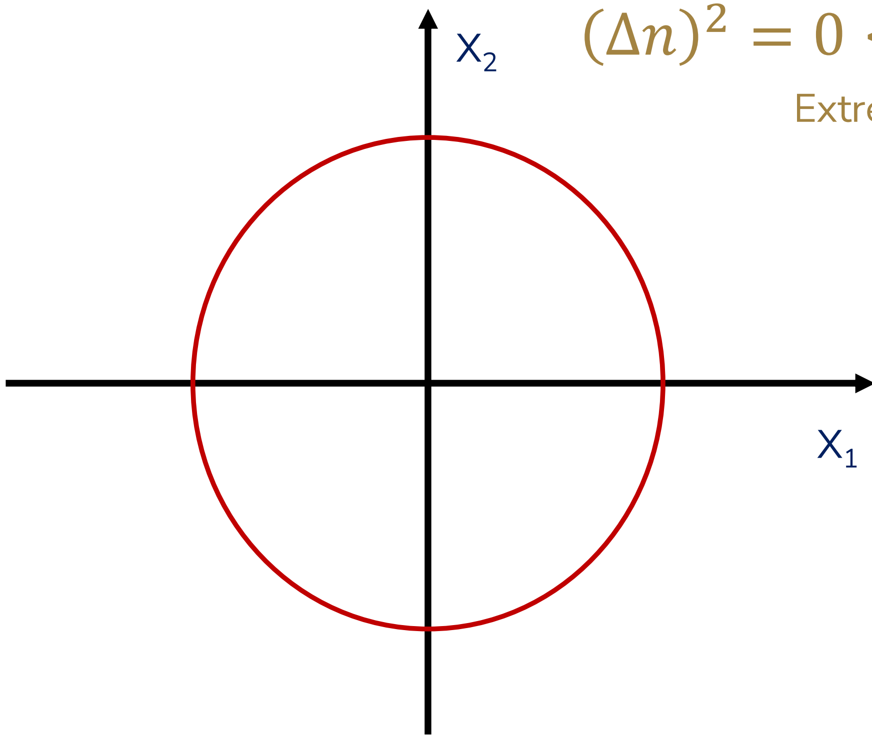
Phase space trajectory

Dynamics of a coherent state



Standard quantum limit to the variance!

Fock state - $|n\rangle$



$$(\Delta n)^2 = 0 < \bar{n}$$

Extreme case of sub-P light

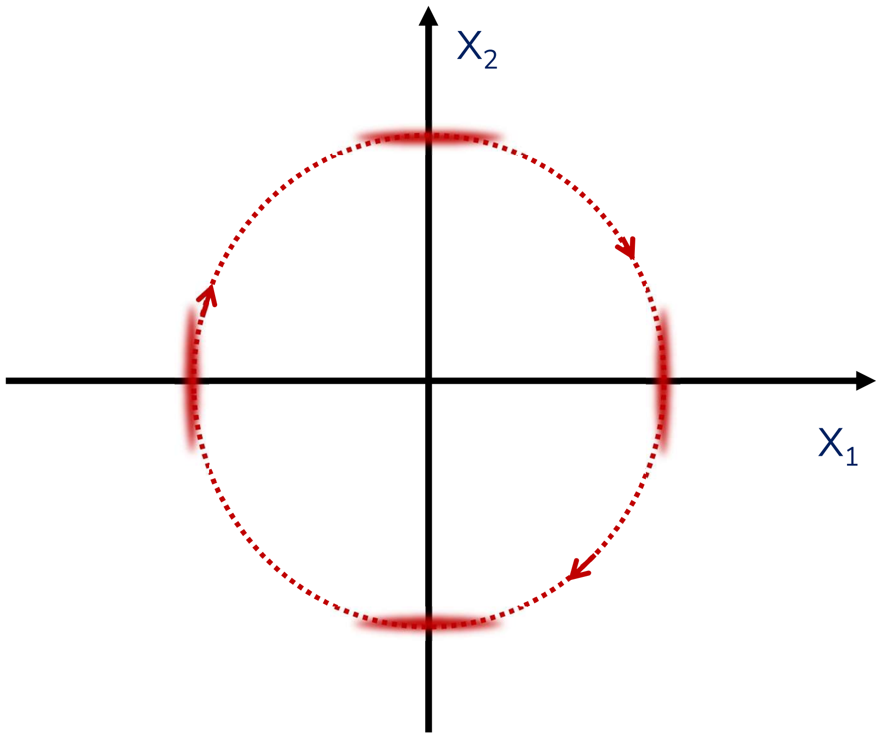
$$\Delta n = 0$$

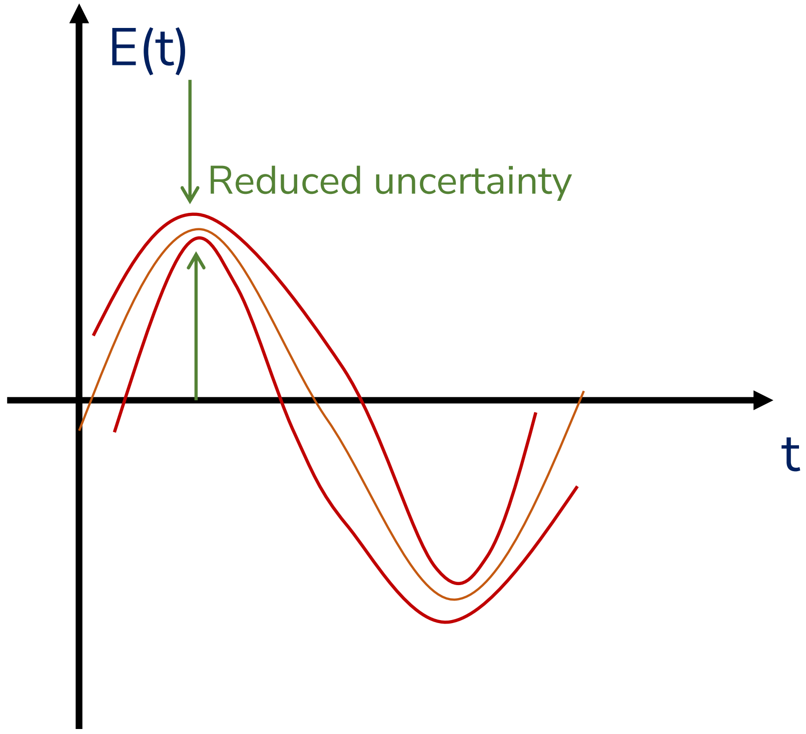
$$\Delta\phi = \infty$$

Within the quantum mechanical description,
It is impossible to measure amplitude and
phase of the EM field "exactly"

$$\Delta X_1 = \Delta X_2 = \sqrt{\frac{1}{2}\left(n + \frac{1}{2}\right)}$$

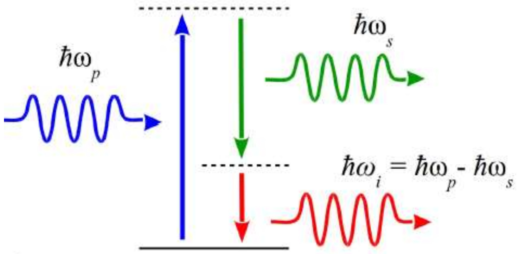
Dynamics of a squeezed state





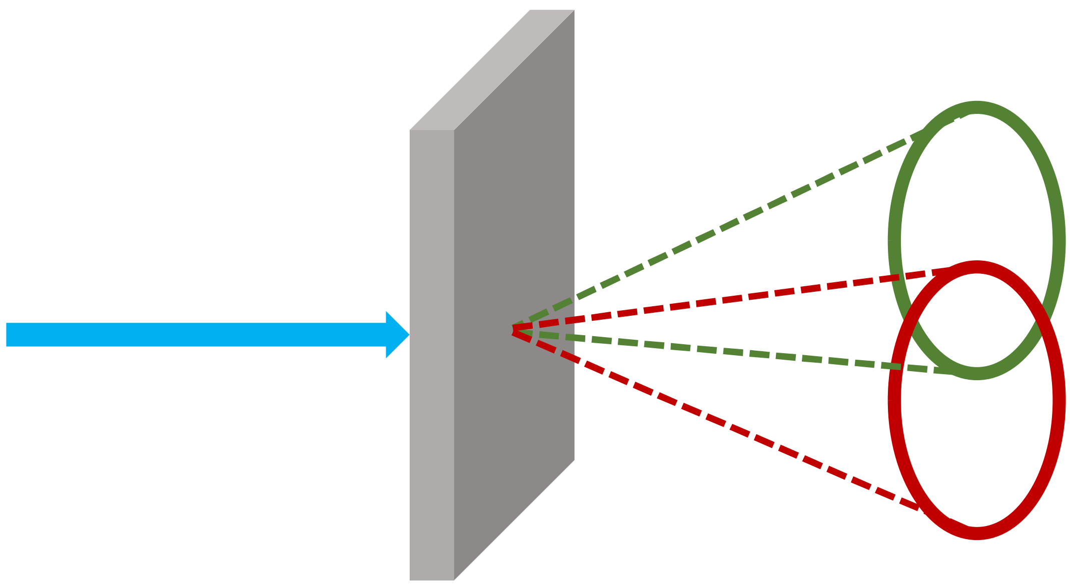
Can beat the standard quantum limit!

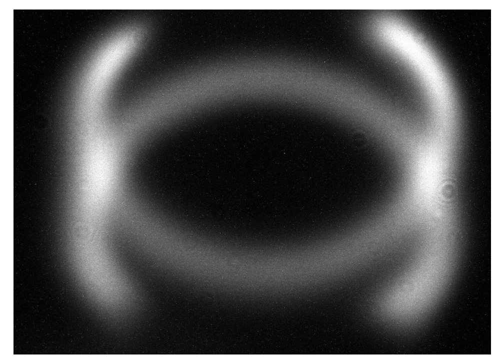
How to generate squeezed light?



Spontaneous parametric downconversion (SPDC)

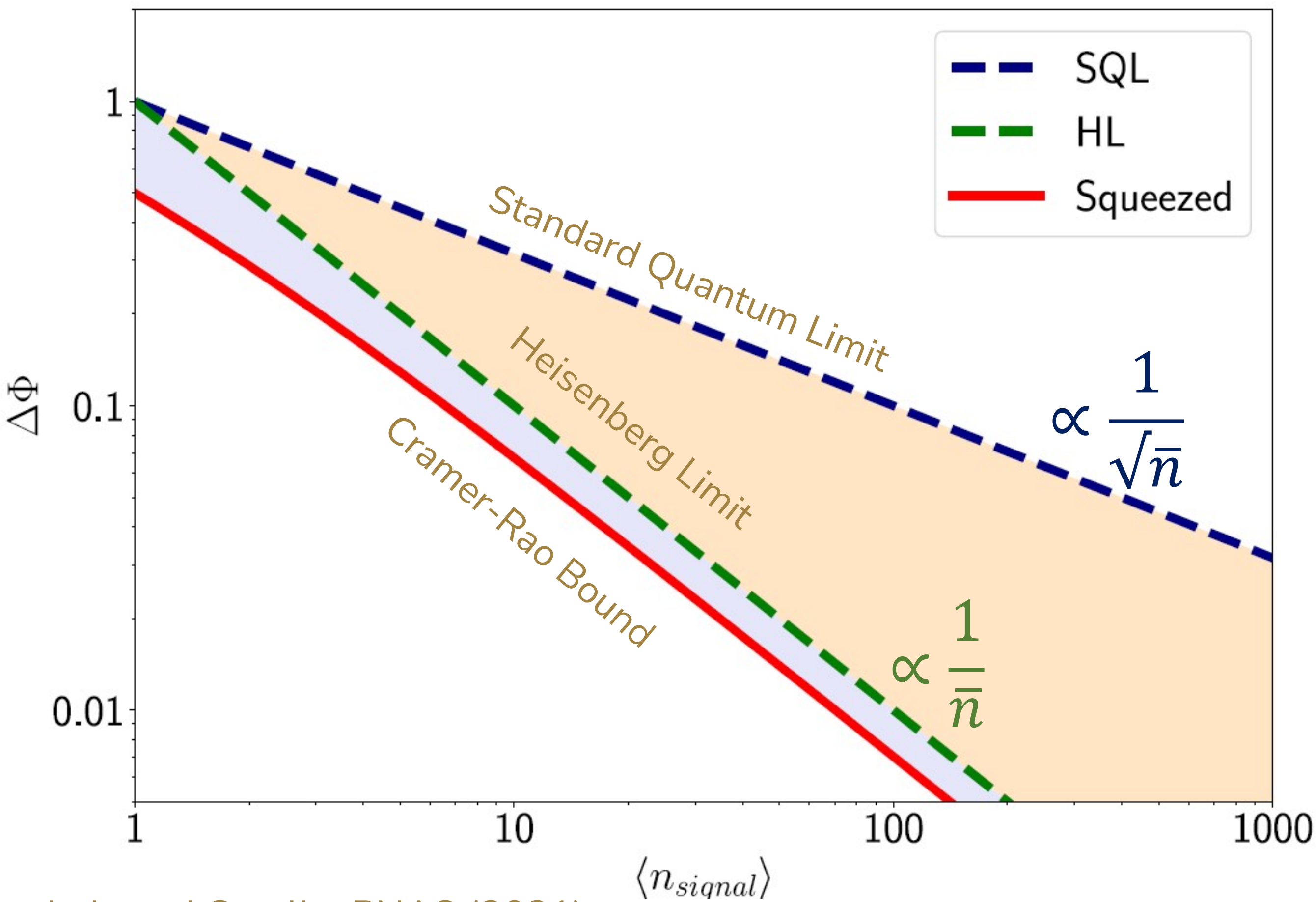
Squeezing parameter: $\xi = 2\chi^{(2)}\sqrt{\bar{n}_{pump}}t$





Quantum entangled photons

Towards quantum advantage

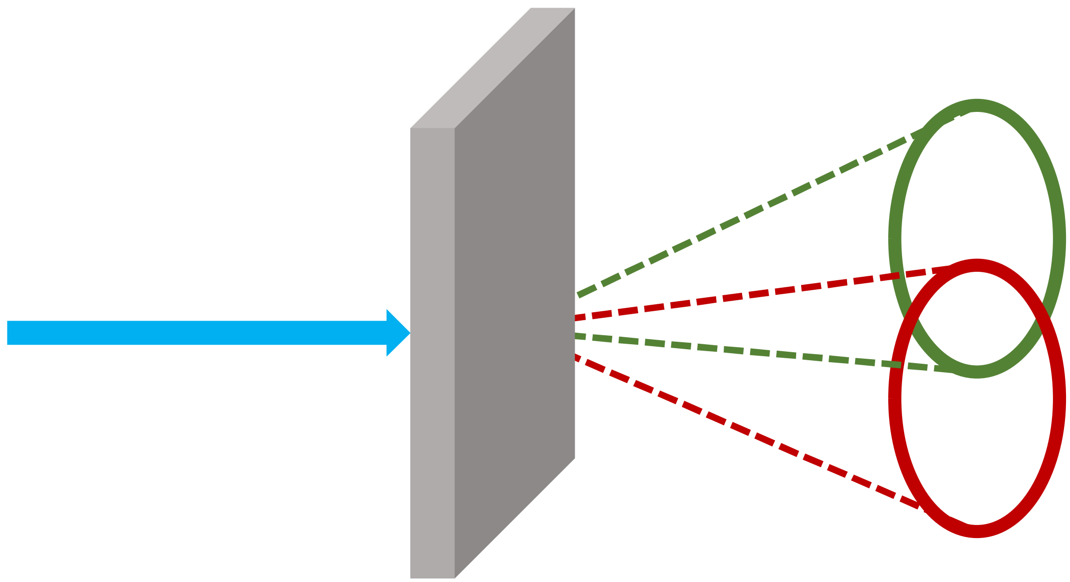


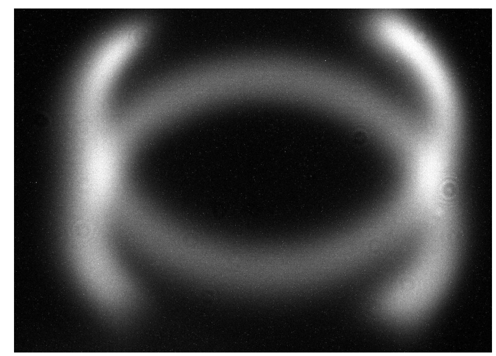
A. R. Srimath Kandada and Cerullo, PNAS (2021)

Outline

- What is quantum light?
    - Basics of photo-detection
    - Intro to quantum mechanical description of light
- Quantum advantage in material spectroscopy
    - Concept of squeezed light
    - How to beat the shot noise limit?
    - Examples
- Emerging perspectives in quantum spectroscopy
    - Intro to quantum entanglement
    - Hong-Ou-Mandel interferometry and dephasing times
    - Quantum process tomography and entanglement in matter

SPDC photons are also quantum entangled



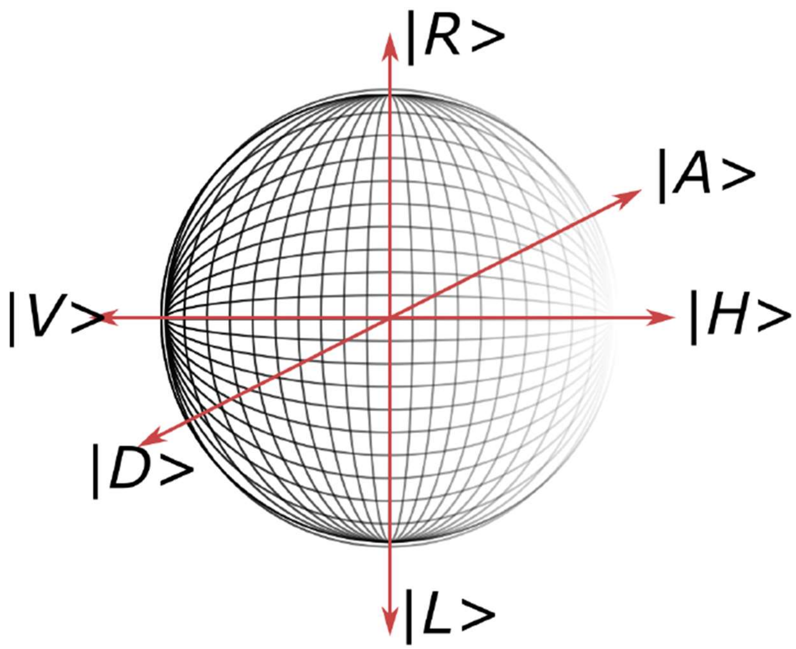


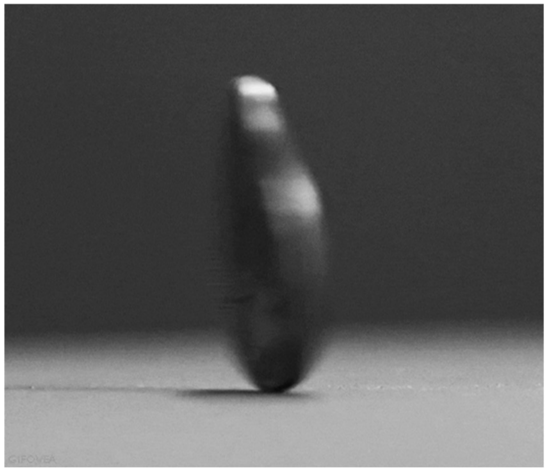
Quantum entangled photons

QUANTUM SUPERPOSITION

$$|\psi\rangle = \alpha_1|0\rangle + \alpha_2|1\rangle$$

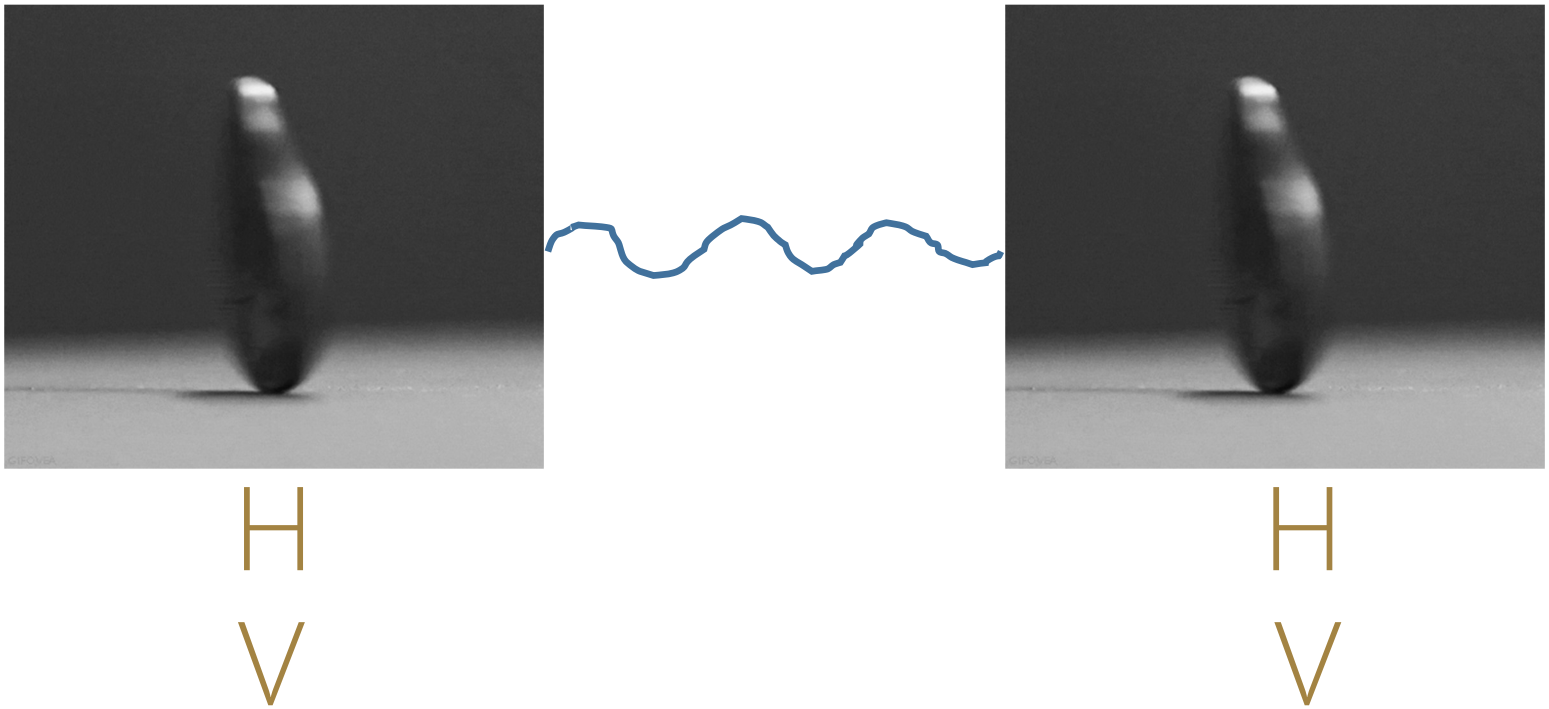
$$|\alpha_1|^2 + |\alpha_2|^2 = 1$$





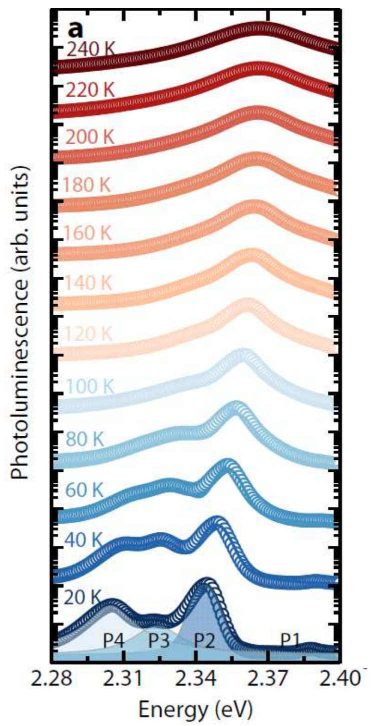
Eg: Polarization of a photon
Spin of an electron

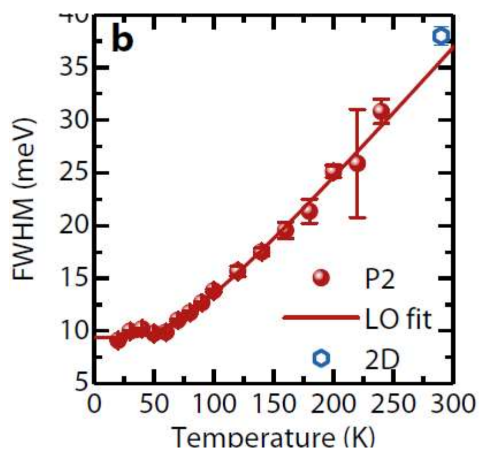
QUANTUM ENTANGLEMENT



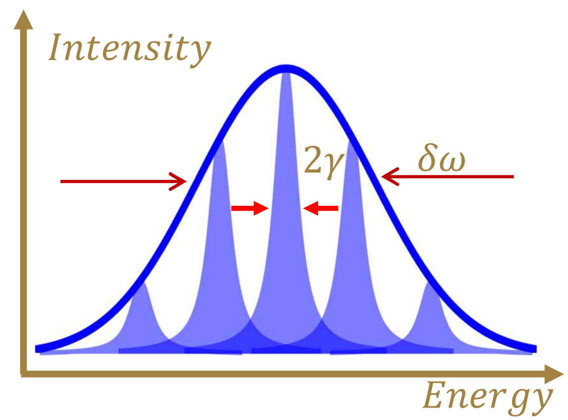
Two systems are in a special case of quantum mechanical superposition called entanglement if the measurement of one system is correlated with the state of the other system in a way that is stronger than correlations in the classical world. In other words, the states of the two systems are *not separable and indistinguishable*.

NOTE: HOW TO MEASURE HOMOGENEOUS LINEWIDTHS?





Neutzner...Kandada,
Phys. Rev. Mater. 2, 064605



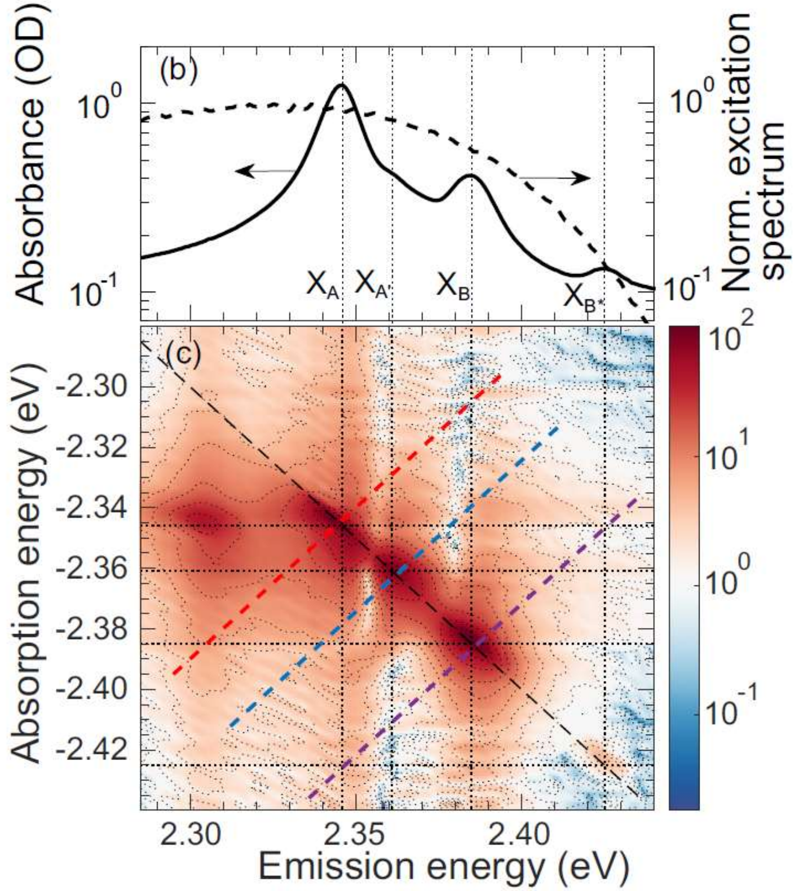
Width defined by dephasing time

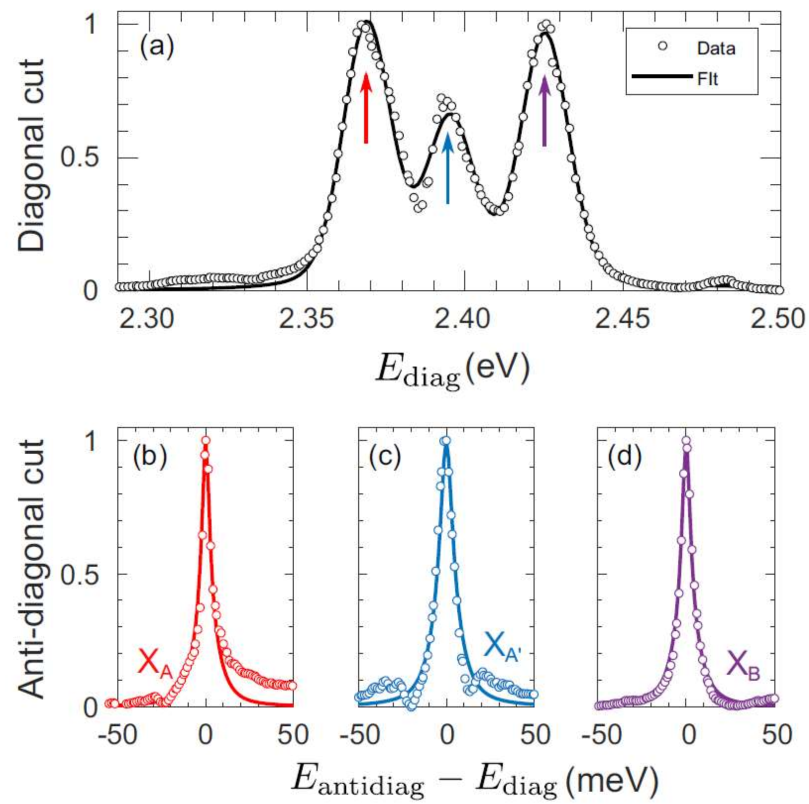
Only in the homogenous limit

$$T_2^{-1} = \Delta^2/\gamma$$

- How to measure the homogenous **linewidth?**

$(PEA)_2PbI_4$: EXCITON LINEWIDTH from 2D SPECTRUM





Thouin..Kandada, Silva, Phys. Rev. Research 2, 034001 (2019)

Photon entanglement

$$|\psi_{\text{in}}\rangle_{ab} = \hat{a}_j^{\dagger}\hat{b}_k^{\dagger}|0\rangle_{ab} = |1;j\rangle_a|1;k\rangle_b$$

a) Polarization

b) Spatial

c) Temporal

d) Spectral

Photon entanglement as material probe

1. What kind of entanglement?

   a) Polarization

   b) Spatial

   c) Temporal

   d) Spectral

2. What is the measurement?

3. What is the material problem to address?

Photon entanglement as material probe

1. What kind of entanglement?

   a) Polarization

   b) Spatial

   c) Temporal

   d) Spectral

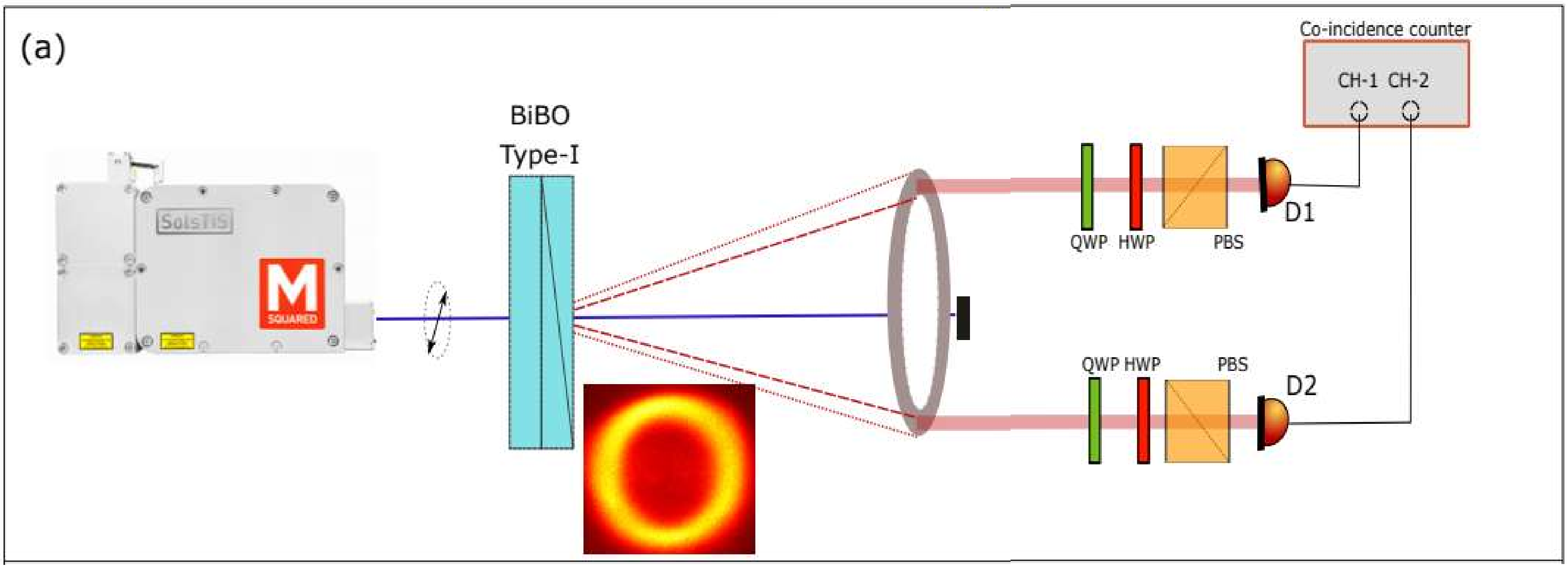
2. What is the measurement?

   Quantum Process Tomography

3. What is the material problem to address?

   Spin entanglement in singlet fission intermediates

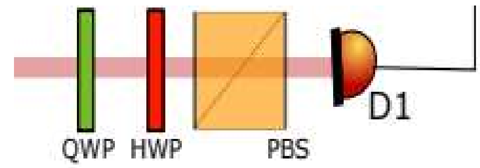
Quantum State Tomography



Phys. Rev. A. 64, 052312

Single qubit Tomography - Polarimetry

Sequence of 4 measurements to determine the polarization of light



$$n_0=\frac{\mathcal{N}}{2}(\langle H|\hat{\rho}|H\rangle+\langle V|\hat{\rho}|V\rangle)=\frac{\mathcal{N}}{2}(\langle R|\hat{\rho}|R\rangle+\langle L|\hat{\rho}|L\rangle)$$

- Half the intensity irrespective of polarization

$$n_1=\mathcal{N}(\langle H|\hat{\rho}|H\rangle)$$
$$=\frac{\mathcal{N}}{2}(\langle R|\hat{\rho}|R\rangle+\langle R|\hat{\rho}|L\rangle+\langle L|\hat{\rho}|R\rangle+\langle L|\hat{\rho}|L\rangle)$$

- Only horizontally polarized light

$$n_2=\mathcal{N}(\langle \overline{D}|\hat{\rho}|\overline{D}\rangle)$$
$$=\frac{\mathcal{N}}{2}(\langle R|\hat{\rho}|R\rangle+\langle L|\hat{\rho}|L\rangle-i\langle L|\hat{\rho}|R\rangle+i\langle R|\hat{\rho}|L\rangle)$$

- Light polarized at 45°

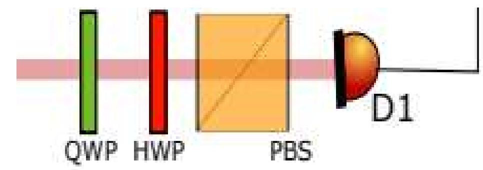
$$n_3=\mathcal{N}(\langle R|\hat{\rho}|R\rangle).$$

- Right circularly polarized light

Phys. Rev. A. 64, 052312

Single qubit Tomography - Polarimetry

Sequence of 4 measurements to determine the polarization of light



Stokes Parameters

$$\mathcal{S}_0 \equiv 2n_0 = \mathcal{N}(\langle R|\hat{\rho}|R\rangle + \langle L|\hat{\rho}|L\rangle),$$

$$\mathcal{S}_1 \equiv 2(n_1 - n_0) = \mathcal{N}(\langle R|\hat{\rho}|L\rangle + \langle L|\hat{\rho}|R\rangle),$$

$$\mathcal{S}_2 \equiv 2(n_2 - n_0) = \mathcal{N}i(\langle R|\hat{\rho}|L\rangle - \langle L|\hat{\rho}|R\rangle),$$

$$\mathcal{S}_3 \equiv 2(n_3 - n_0) = \mathcal{N}(\langle R|\hat{\rho}|R\rangle - \langle L|\hat{\rho}|L\rangle).$$

- Half the intensity irrespective of polarization
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Phys. Rev. A. 64, 052312

Single qubit Tomography - Polarimetry

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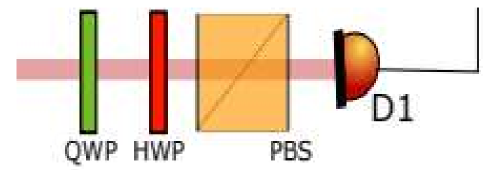

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$$\mathcal{S}_3 \equiv 2(n_3 - n_0) = \mathcal{N}(\langle R|\hat{\rho}|R\rangle - \langle L|\hat{\rho}|L\rangle).$$

Density matrix, which quantifies the projection of the state onto itself has all the relevant information of the quantum state.

Density Matrix

$$\hat{\rho} = \frac{1}{2}\sum^{3} S_i \hat{\sigma}_i$$

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Phys. Rev. A. 64, 052312

Multi qubit Tomography

$$\hat{\rho} = \frac{1}{2^n} \sum_{i_1, i_2, \ldots, i_n = 0}^{3} r_{i_1, i_2, \ldots, i_n} \hat{\sigma}_{i_1} \otimes \hat{\sigma}_{i_2} \otimes \cdots \otimes \hat{\sigma}_{i_n},$$

$$\hat{\rho} = \frac{1}{2} \sum_{i=0}^{3} \frac{\mathcal{S}_i}{\mathcal{S}_0} \hat{\sigma}_i$$

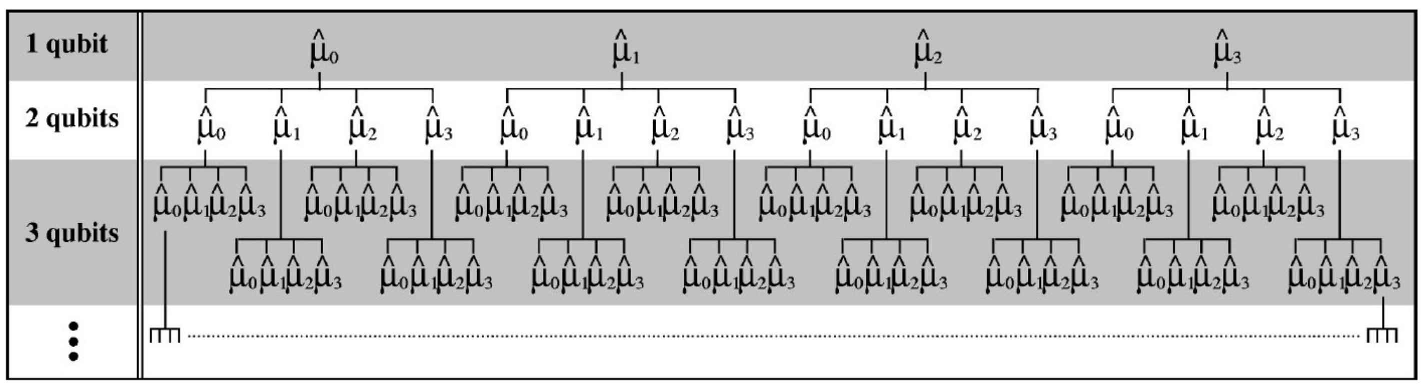
2-qubit measurement: $\hat{\mu}_i \otimes \hat{\mu}_j$

$$\hat{\mu}_0 = |H\rangle\langle H| + |V\rangle\langle V|$$

$$\hat{\mu}_1 = |H\rangle\langle H|$$

$$\hat{\mu}_2 = |\bar{D}\rangle\langle \bar{D}|$$

$$\hat{\mu}_3 = |R\rangle\langle R|$$



Phys. Rev. A. 64, 052312

Two qubit Tomography

$$|\psi^{(2)}_{proj}(h_1,q_1,h_2,q_2)\rangle=|\psi^{(1)}_{proj}(h_1,q_1)\rangle\otimes|\psi^{(1)}_{proj}(h_2,q_2)\rangle$$

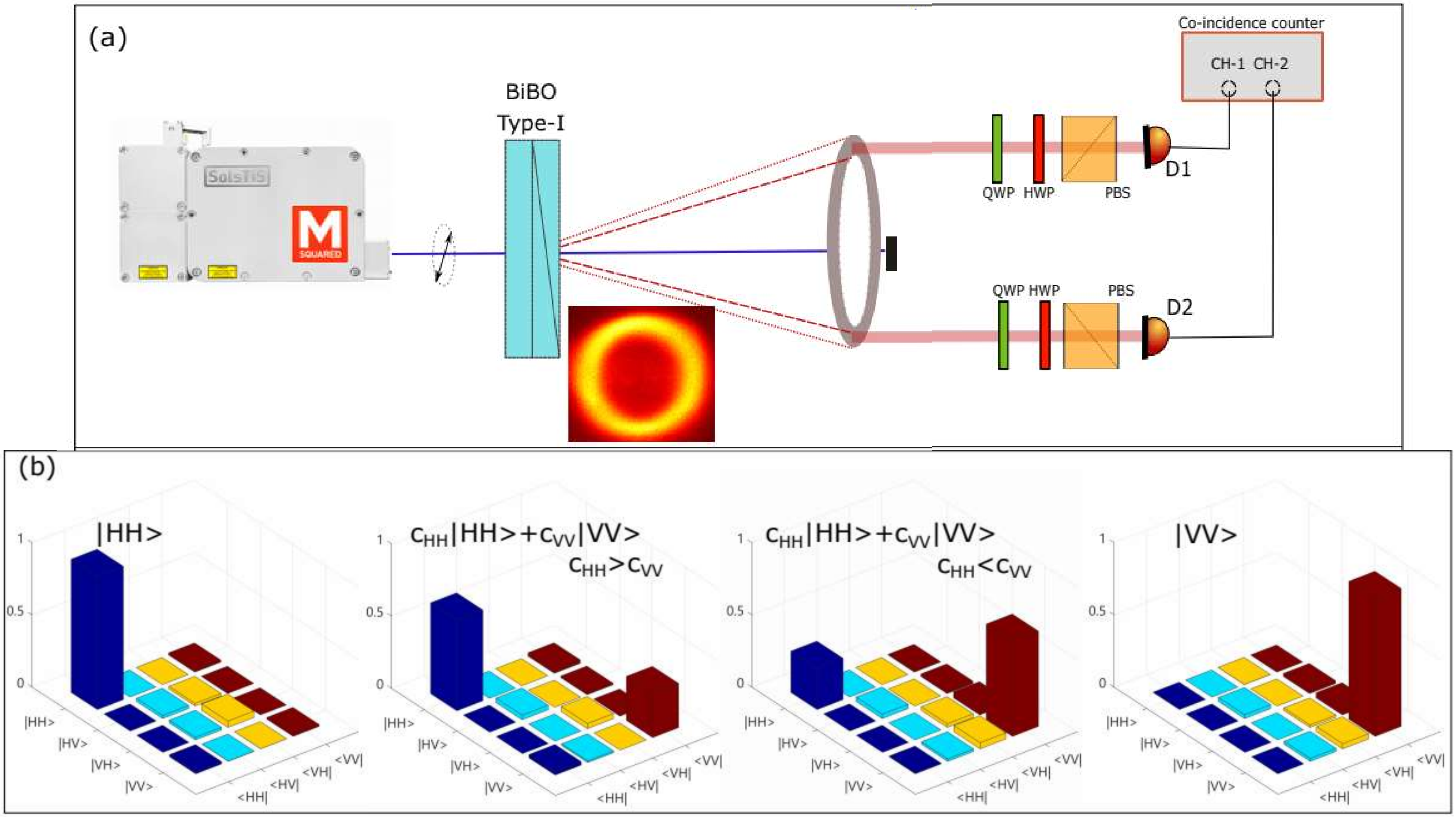
Measurement

$$n_\nu=\mathcal{N}\langle\psi_\nu|\hat{\rho}|\psi_\nu\rangle$$

$$\hat{\rho}=\left(\sum_{\nu=1}^{16}\hat{M}_\nu n_\nu\right)\Big/\left(\sum_{\nu=1}^{4}n_\nu\right)$$

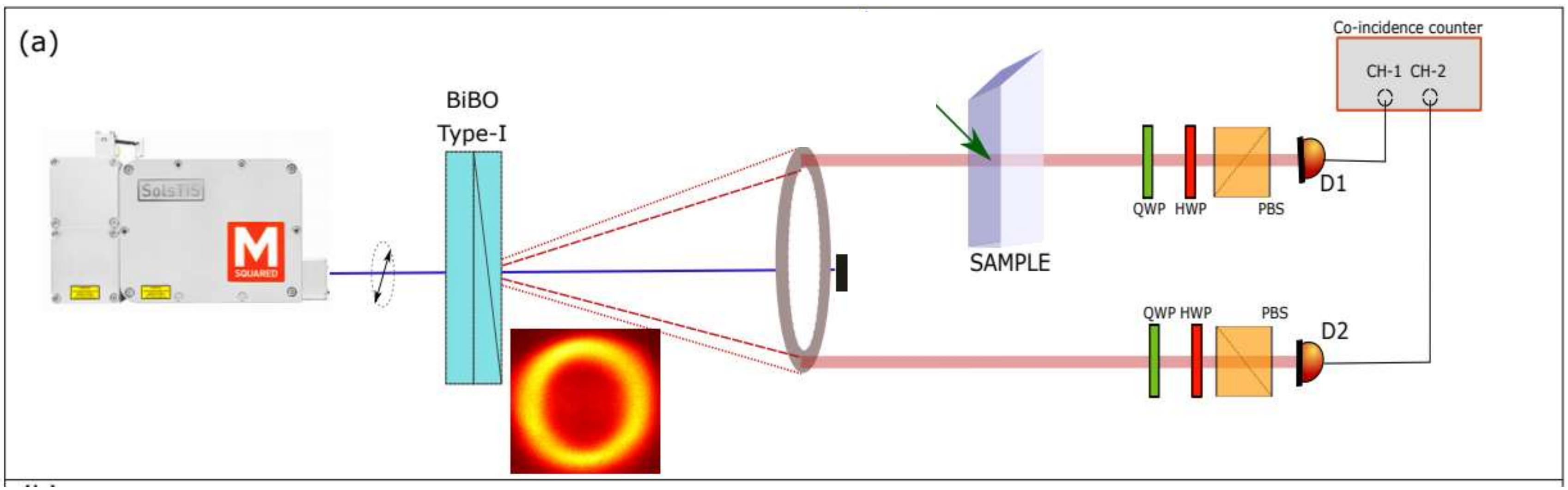
ν	Mode 1	Mode 2	h_1	q_1	h_2	q_2
1	$\|H\rangle$	$\|H\rangle$	45°	0	45°	0
2	$\|H\rangle$	$\|V\rangle$	45°	0	0	0
3	$\|V\rangle$	$\|V\rangle$	0	0	0	0
4	$\|V\rangle$	$\|H\rangle$	0	0	45°	0
5	$\|R\rangle$	$\|H\rangle$	22.5°	0	45°	0
6	$\|R\rangle$	$\|V\rangle$	22.5°	0	0	0
7	$\|D\rangle$	$\|V\rangle$	22.5°	45°	0	0
8	$\|D\rangle$	$\|H\rangle$	22.5°	45°	45°	0
9	$\|D\rangle$	$\|R\rangle$	22.5°	45°	22.5°	0
10	$\|D\rangle$	$\|D\rangle$	22.5°	45°	22.5°	45°
11	$\|R\rangle$	$\|D\rangle$	22.5°	0	22.5°	45°
12	$\|H\rangle$	$\|D\rangle$	45°	0	22.5°	45°
13	$\|V\rangle$	$\|D\rangle$	0	0	22.5°	45°
14	$\|V\rangle$	$\|L\rangle$	0	0	22.5°	90°
15	$\|H\rangle$	$\|L\rangle$	45°	0	22.5°	90°
16	$\|R\rangle$	$\|L\rangle$	22.5°	0	22.5°	90°

Quantum Process Tomography of biphoton state



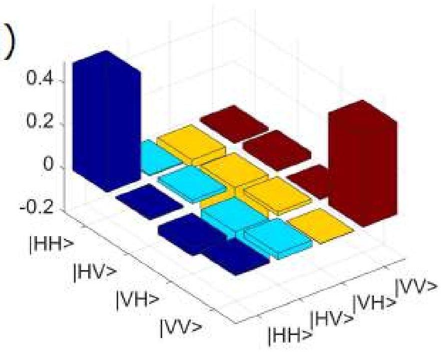
Quantum Process Tomography of biphoton state

Sample interaction with one of the photons



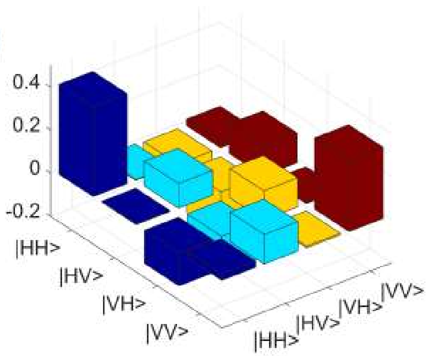
Sample: Quarter Wave Plate

(a)



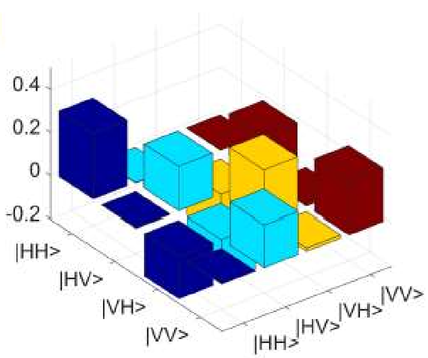
Θ = 0º

(b)

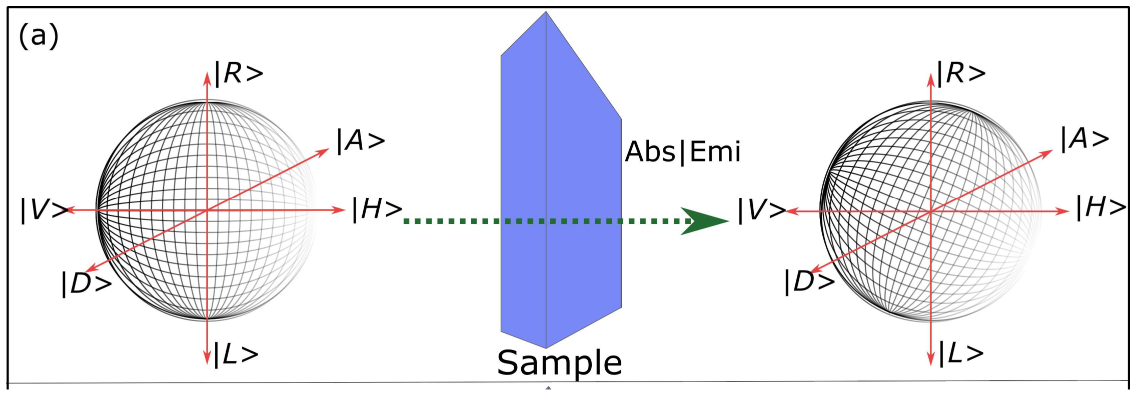


Θ = 22.5º

(c)

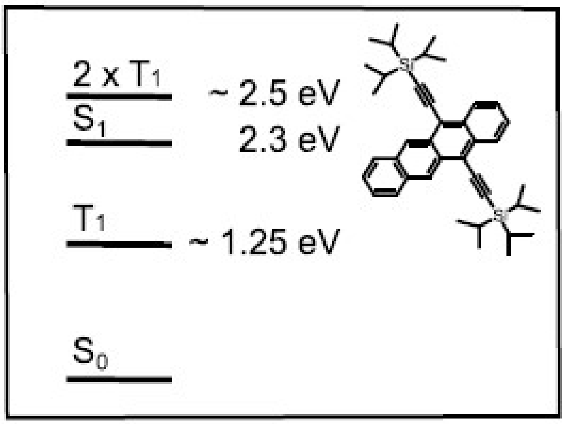


Θ = 45º

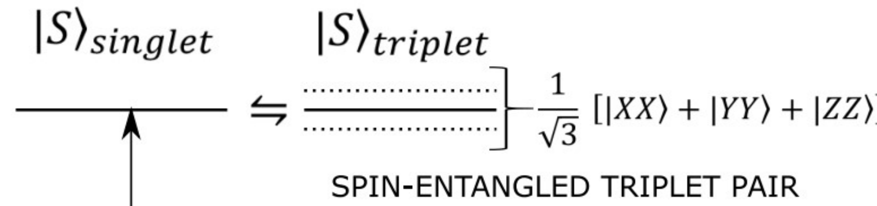


Changes in the density matrix due to Unitary transformation of the biphoton state

Sample: TIPS-tetracene



Stern et al, PNAS 112, 7656
Thanks to John Anthony!



Eigen functions for a pair of spins

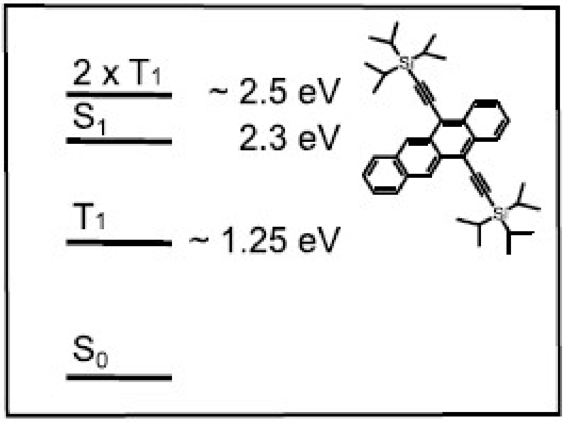
ZERO FIELD	HIGH MAGNETIC FIELD
$\|X\rangle = \frac{1}{\sqrt{2}}[\|\alpha\alpha\rangle - \|\beta\beta\rangle]$	$\|0\rangle = \|Z\rangle$
$\|Y\rangle = \frac{i}{\sqrt{2}}[\|\alpha\alpha\rangle + \|\beta\beta\rangle]$	$\|1\rangle = \|\alpha\alpha\rangle$
$\|Z\rangle = \frac{1}{\sqrt{2}}[\|\alpha\beta\rangle + \|\beta\alpha\rangle]$	$\|2\rangle = \|\beta\beta\rangle$

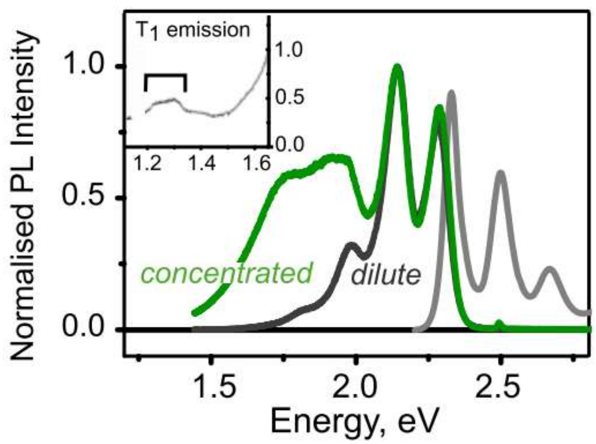
R. E. Merrifield, The Journal of Chemical Physics 48, 4318 (1968)

"The theory presented here cannot be regarded as confirmed until detailed calculations of field dependence and line shapes have been carried out and compared with experiment."

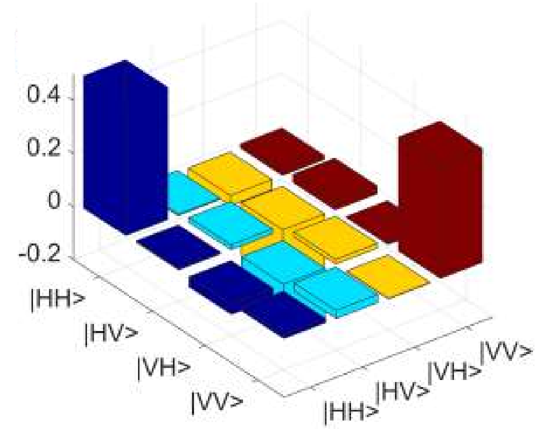
- Can quantum light a unique fresh perspective of the nature of the correlated triplets?

Sample: TIPS-tetracene

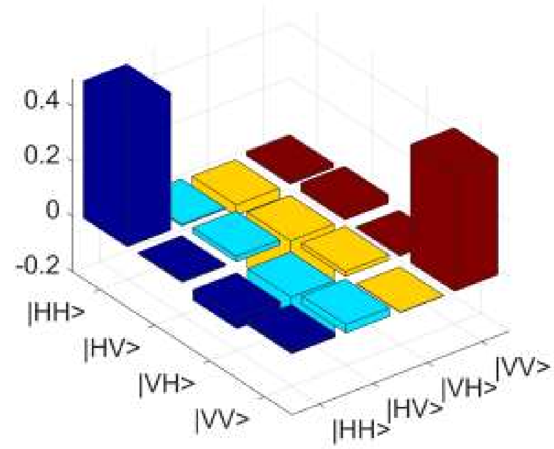




Stern et al, PNAS 112, 7656

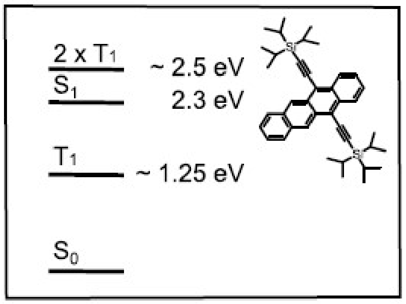


WITH SAMPLE IN THE PATH

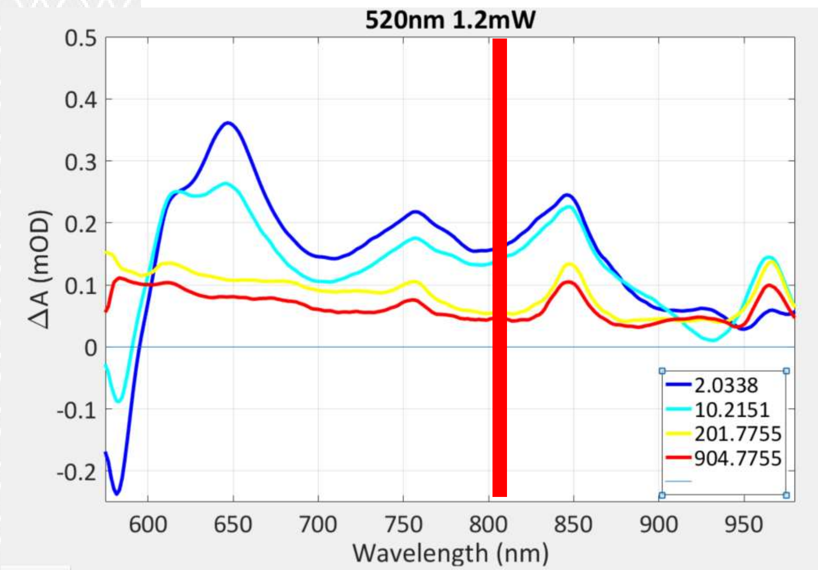


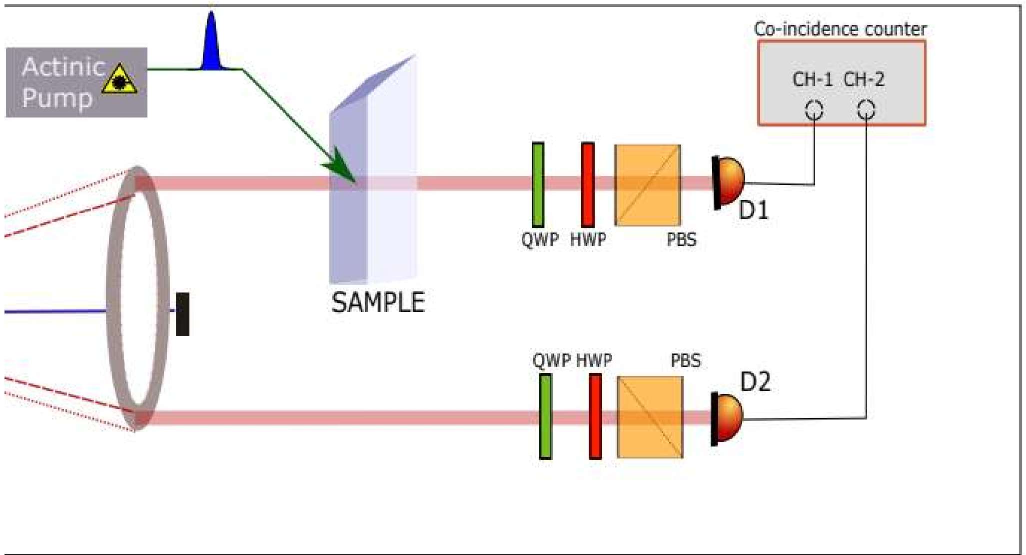
NO SAMPLE IN THE PATH

Sample: TIPS-tetracene



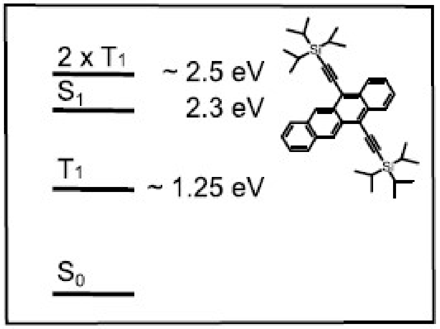
Transient Absorption





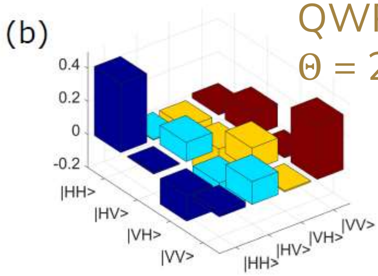
- Energy of the biphoton is resonant with the excited state absorption of the (TT) – intermediate of singlet fission.
- We photo-excite the sample with 80 MHz train of pulses at 520 nm to generate a quasi-steady state population of (TT)

Sample: TIPS-tetracene

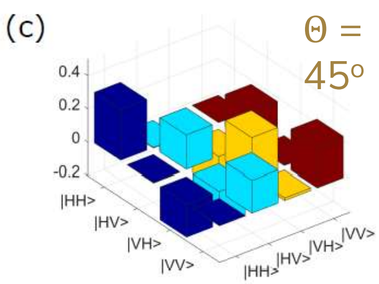


Energy of the biphoton is resonant with the excited state absorption of the (TT) – intermediate of singlet fission.

QWP
Θ = 22.5º

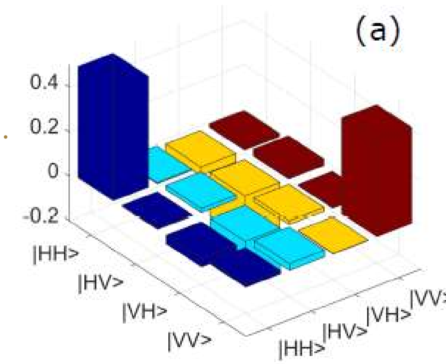


Θ = 45º

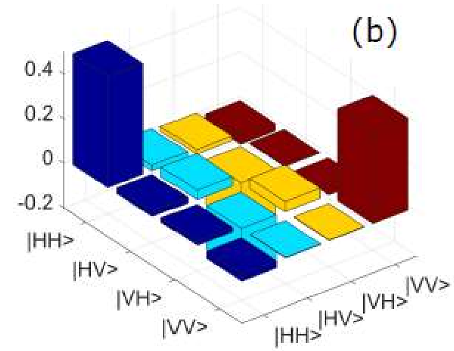


The transformation is equivalent to a unitary transformation dictated by the scattering matrix (related to coherence) of (TT)

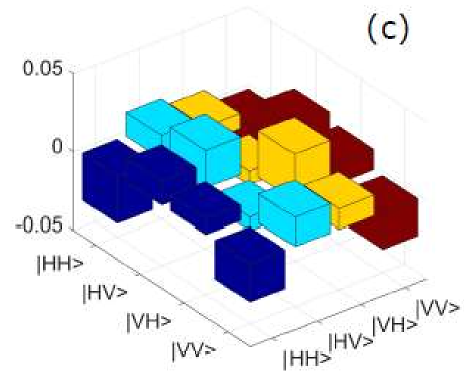
ρ (no pump).



ρ (pump).



Δρ

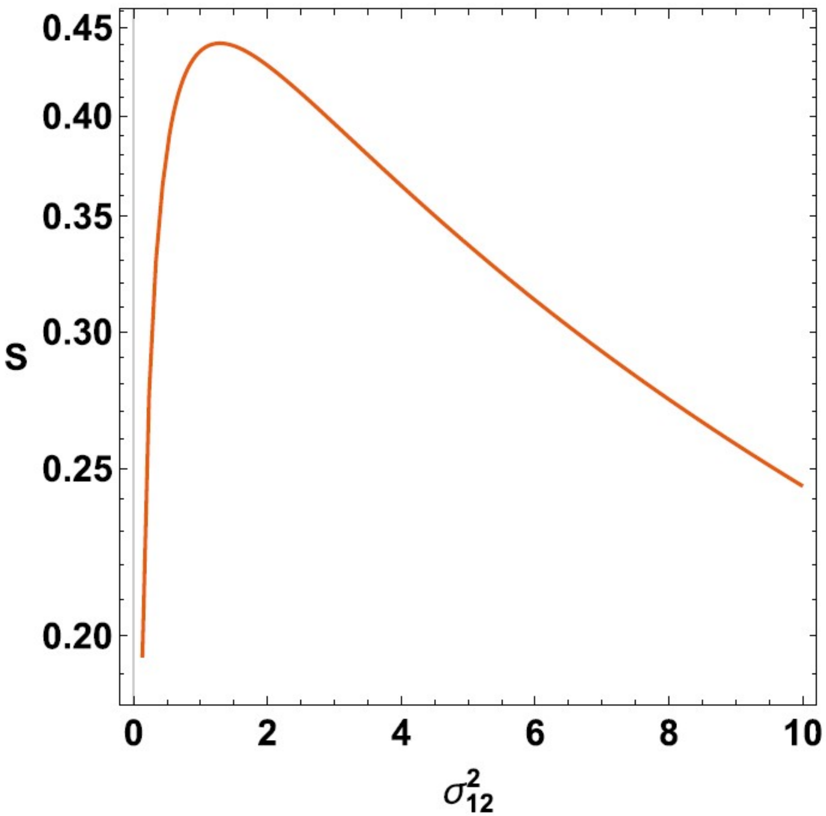


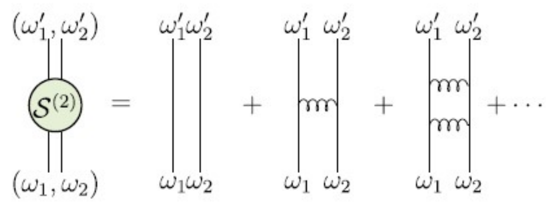
Outline

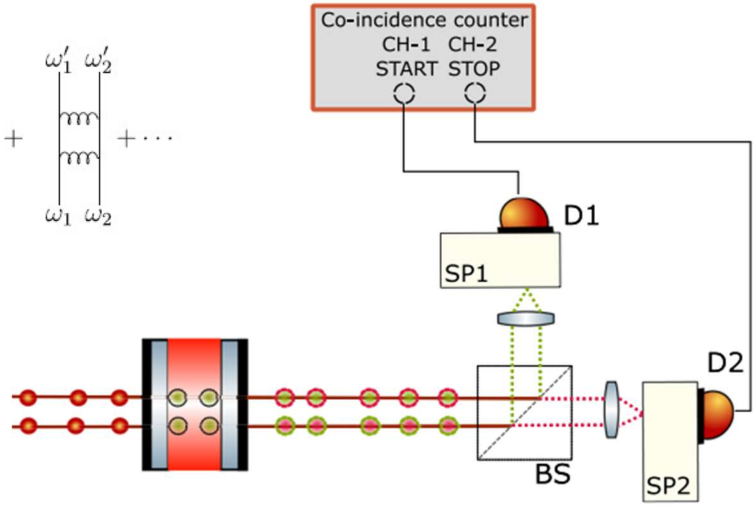
- What is quantum light?
  - Basics of photo-detection
  - Intro to quantum mechanical description of light
- Quantum advantage in material spectroscopy
  - Concept of squeezed light
  - How to beat the shot noise limit?
  - Examples
- Emerging perspectives in quantum spectroscopy
  - Intro to quantum entanglement
  - Hong-Ou-Mandel interferometry and dephasing times
  - Quantum process tomography and entanglement in matter

ENTANGLEMENT ENTROPY TO PROBE BATH FLUCTUATIONS

J. Chem. Phys. 150, 184106





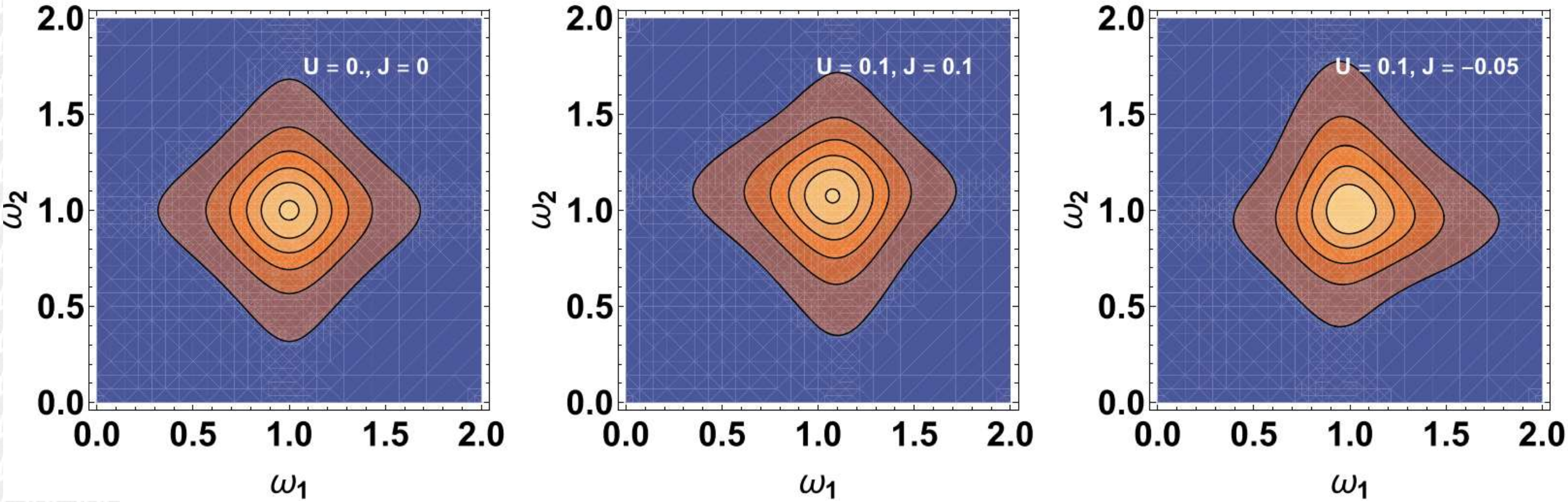


S - correlated to the degree of entanglement

In the limit of slow fluctuations, the entanglement entropy depends on the magnitude of the bath fluctuations and reaches a maximum.

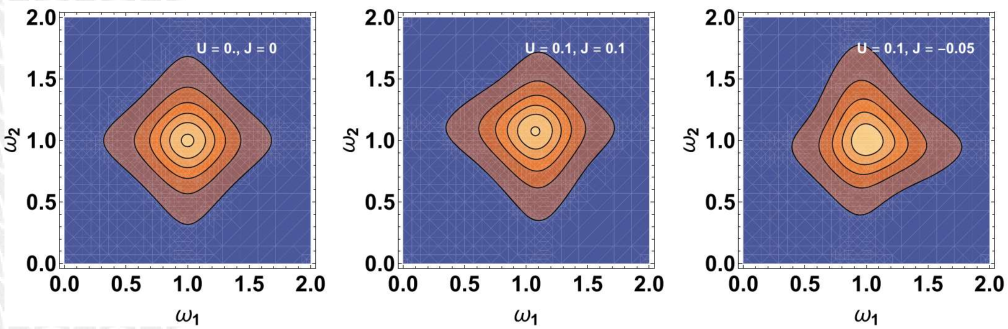
EXCITONIC INTERACTIONS VIA PHOTON ENTANGLEMENT

$$H_{ex} = E_x(\sigma_{z1} + \sigma_{z2} + 1) + J(\sigma_1^+\sigma_2^- + \sigma_2^+\sigma_1^-) + U\,(\sigma_{z1} + 1/2)(\sigma_{z2} + 1/2)$$



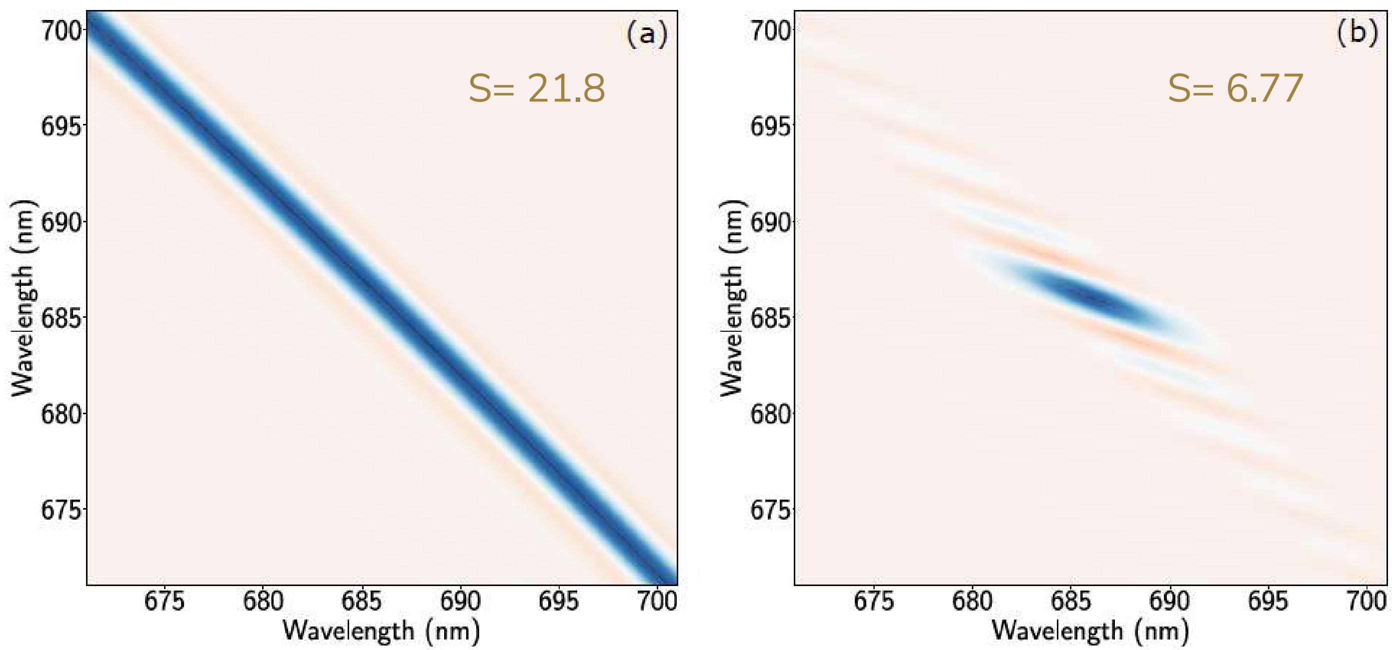
J. Chem. Phys 152, 071101 (2020)

EXCITONIC INTERACTIONS VIA PHOTON ENTANGLEMENT

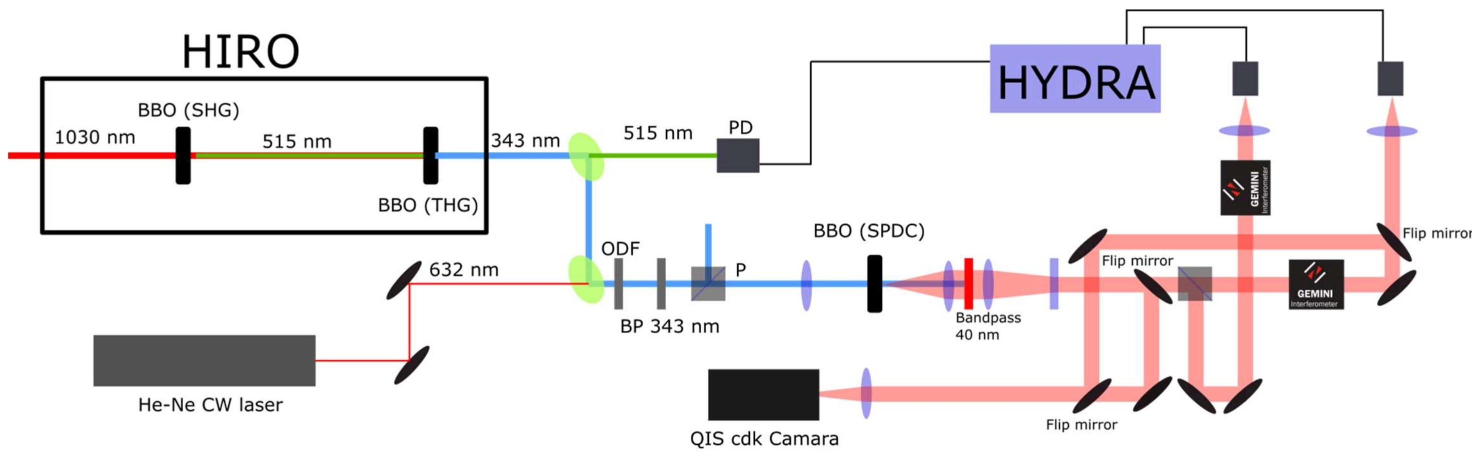


J. Chem. Phys 152, 071101 (2020)

Spectrally broadband entangled photons for material spectroscopy – In progress!



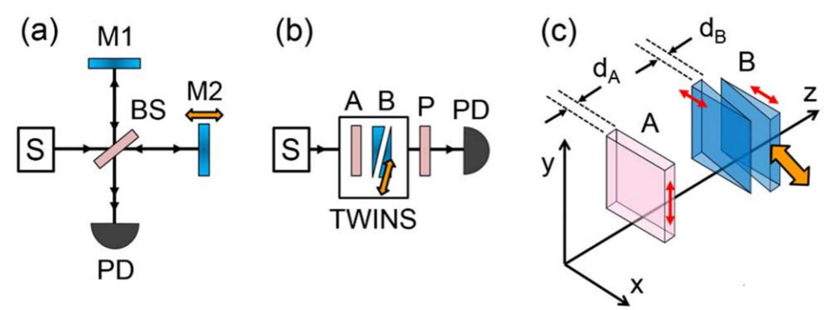
Measurement of Joint Spectral Amplitude using TWINS



Concept behind TWINS:

(a) Equivalent scheme of a Michelson Interferometers: Double-sided orange arrows indicate the moving optics. S, light source; BS, beam splitter; M1, fixed mirror; M2, scanning mirror; PD, photodetector.

(b) a simplified version of the TWINS interferometer. A: birefringent BBO plate, B: BBO wedges, with one on of them on a scanning stage.



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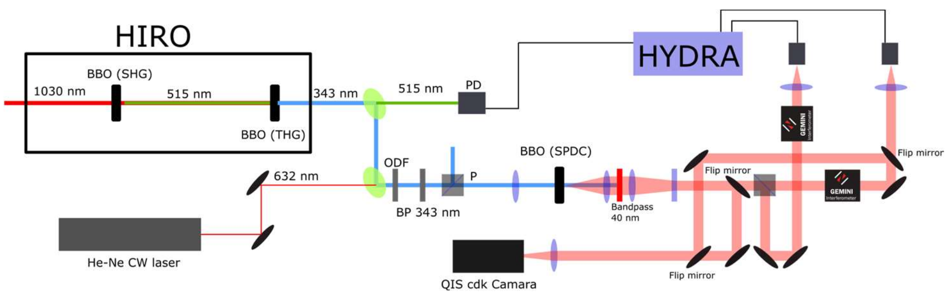
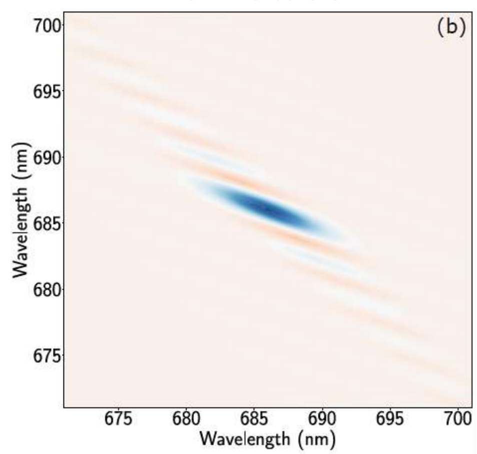
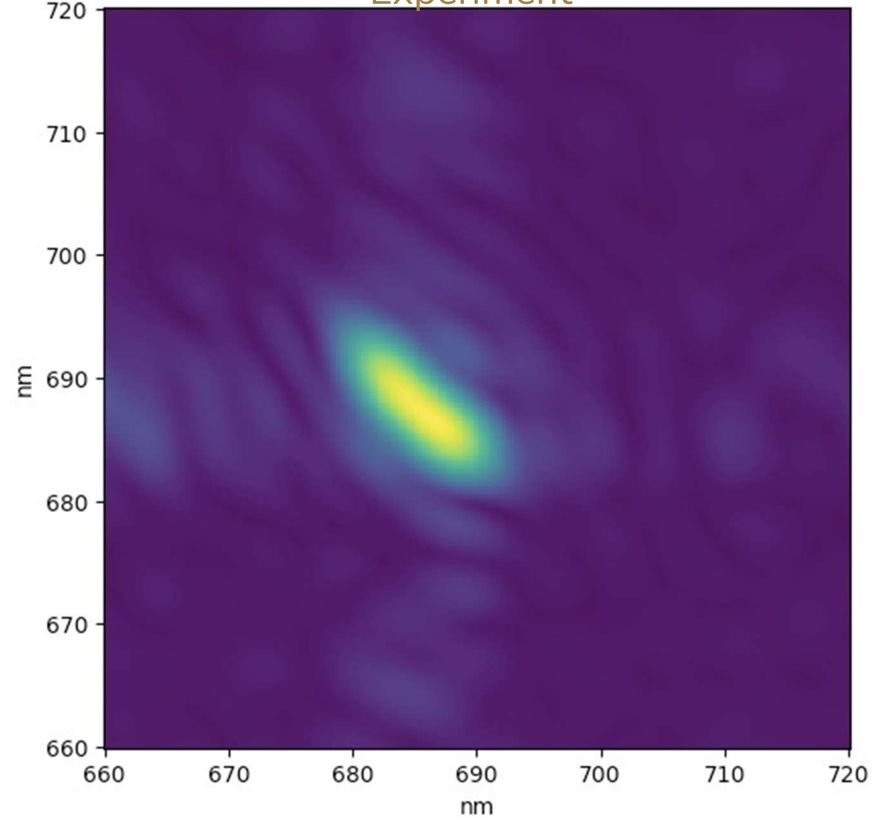


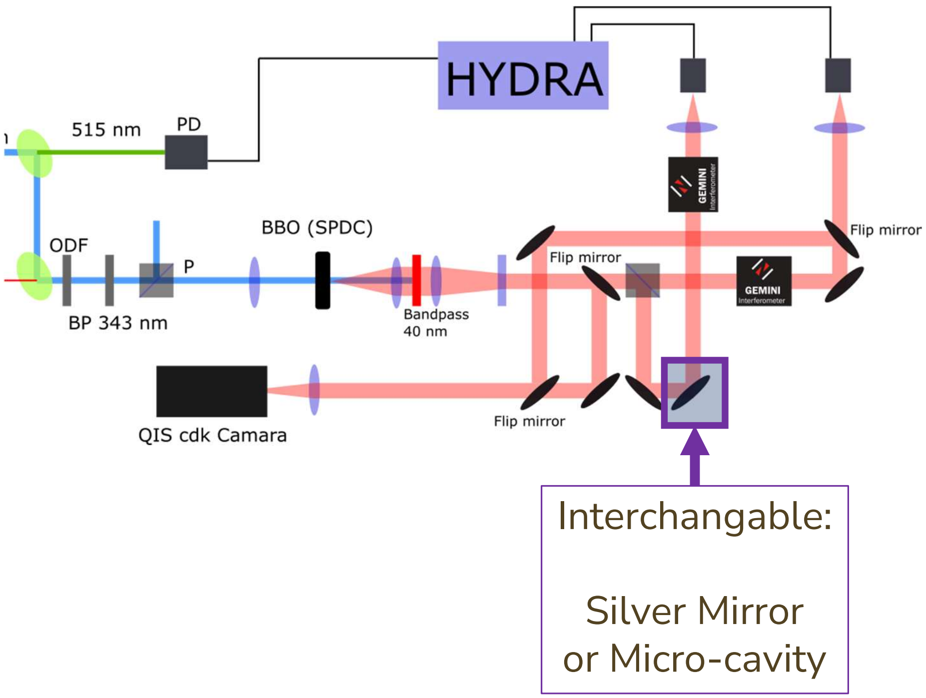
Simulation

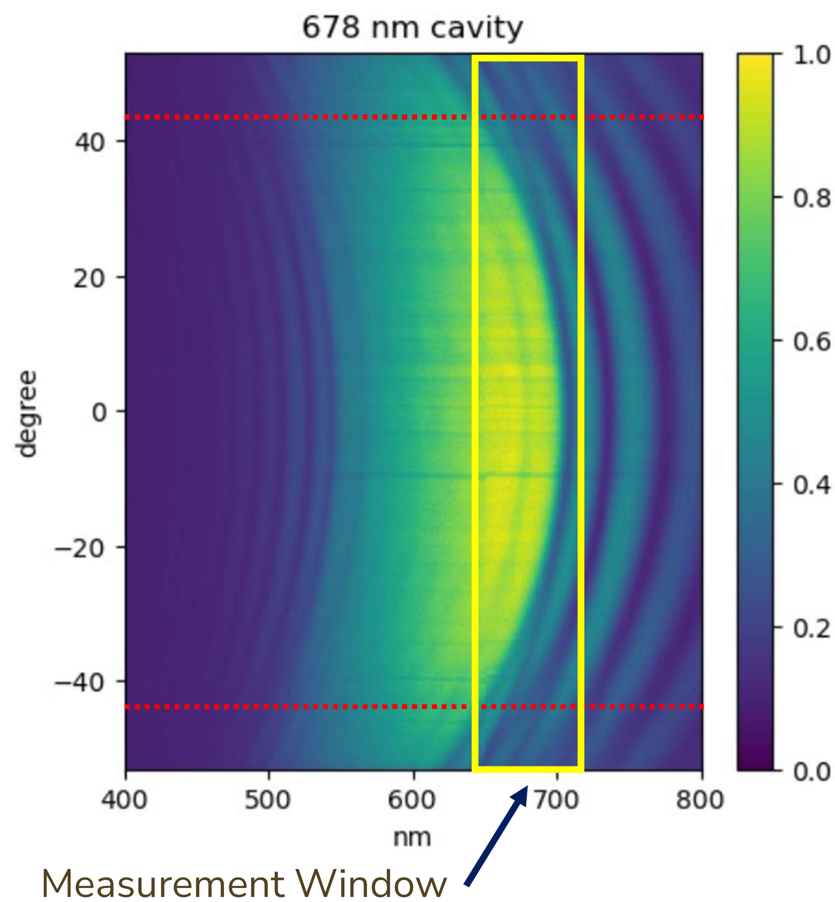


Experiment



JSA as a probe: Cavity at 45^{O} in the path of one of the photons





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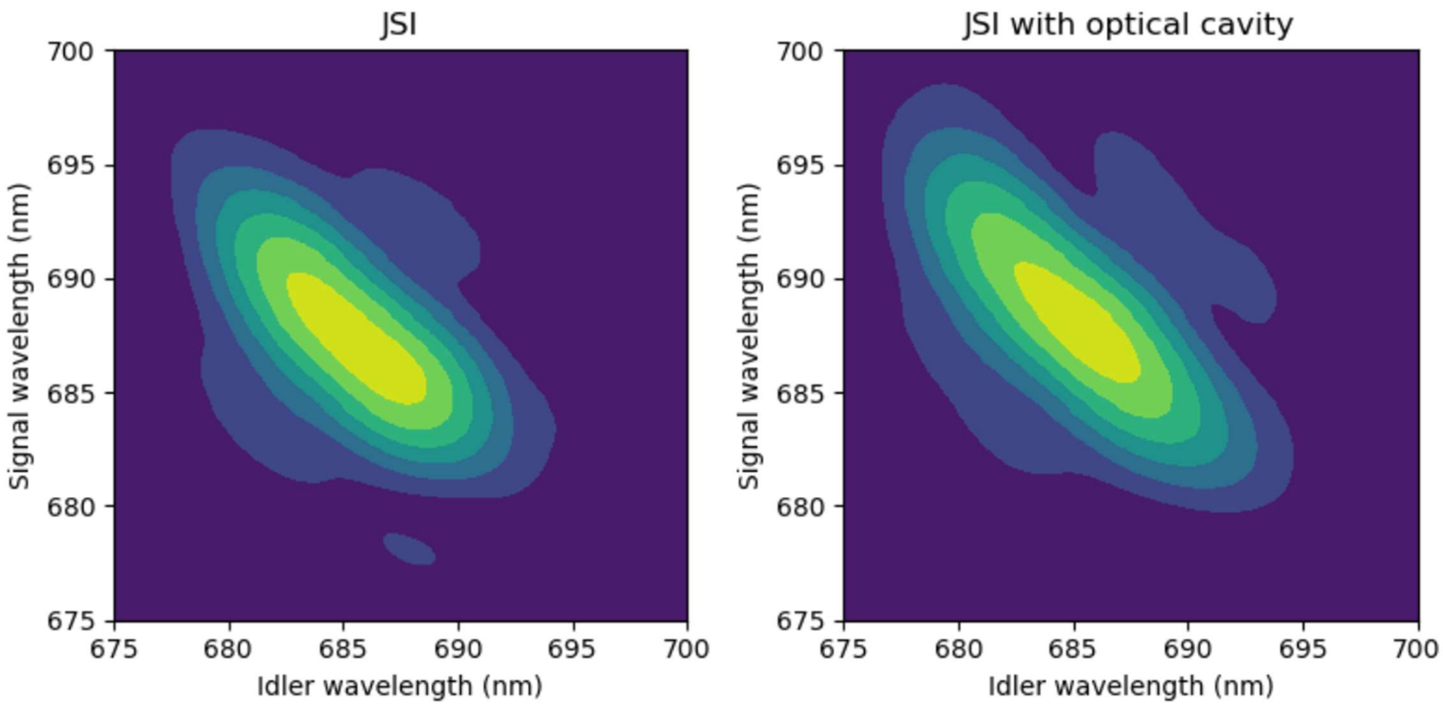

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