Australian Research Council Centre of Excellence in exciton science

Spin Dynamics in Singlet Fission

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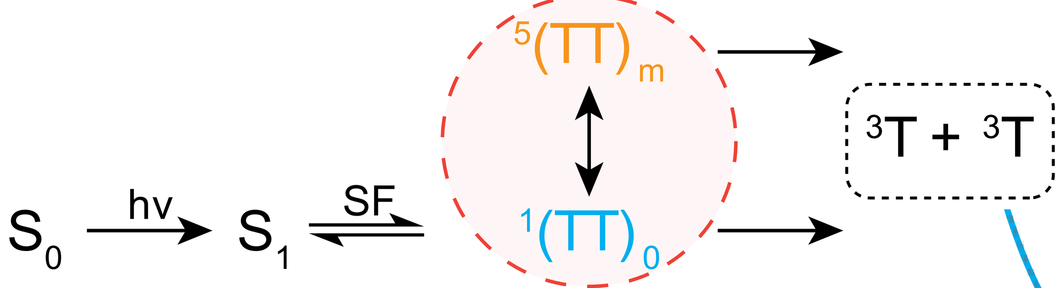
Singlet fission in molecular dimers

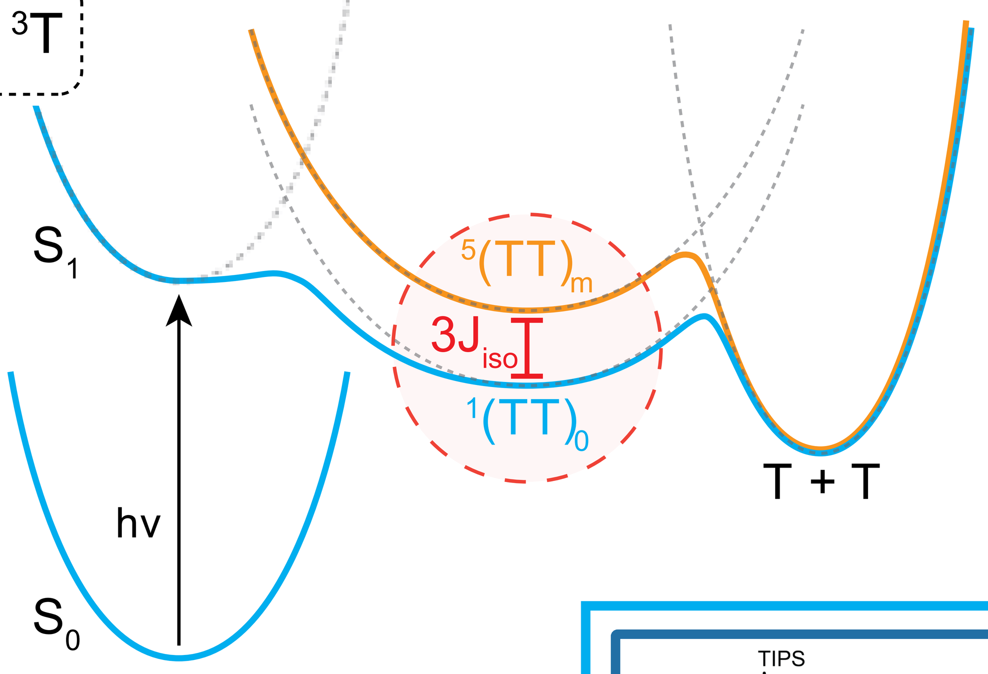


Singlet fission: transition from a singlet exciton to coupled triplet pair ^{1}(TT)$_0$

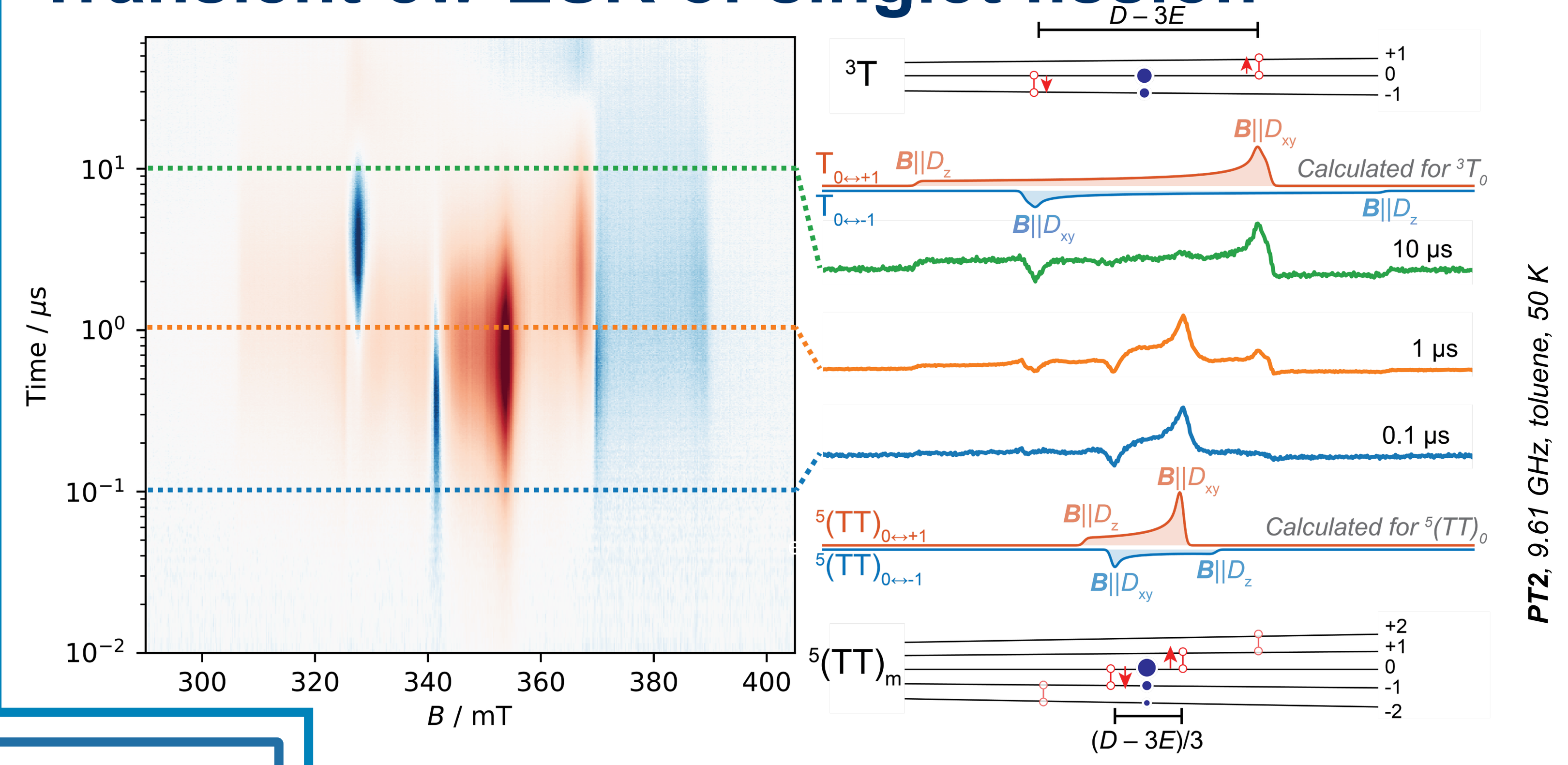
- ^{1}(TT)$_0$ can *dephase* to $^{S(S+1)}$(TT)$_m$
- ^{n}(TT)$_m$ can *dissociate* to free triplets

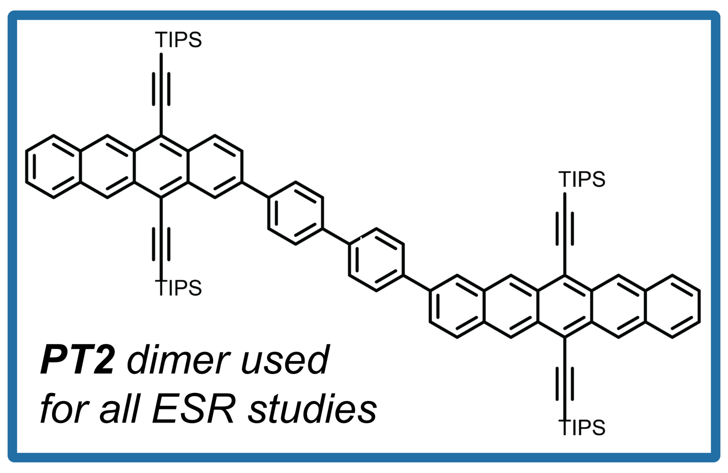
Opportunities:

- Downconversion improves photovoltaics
- Well-defined photogenerated spin states for quantum information, DNP



Transient cw-ESR of singlet fission





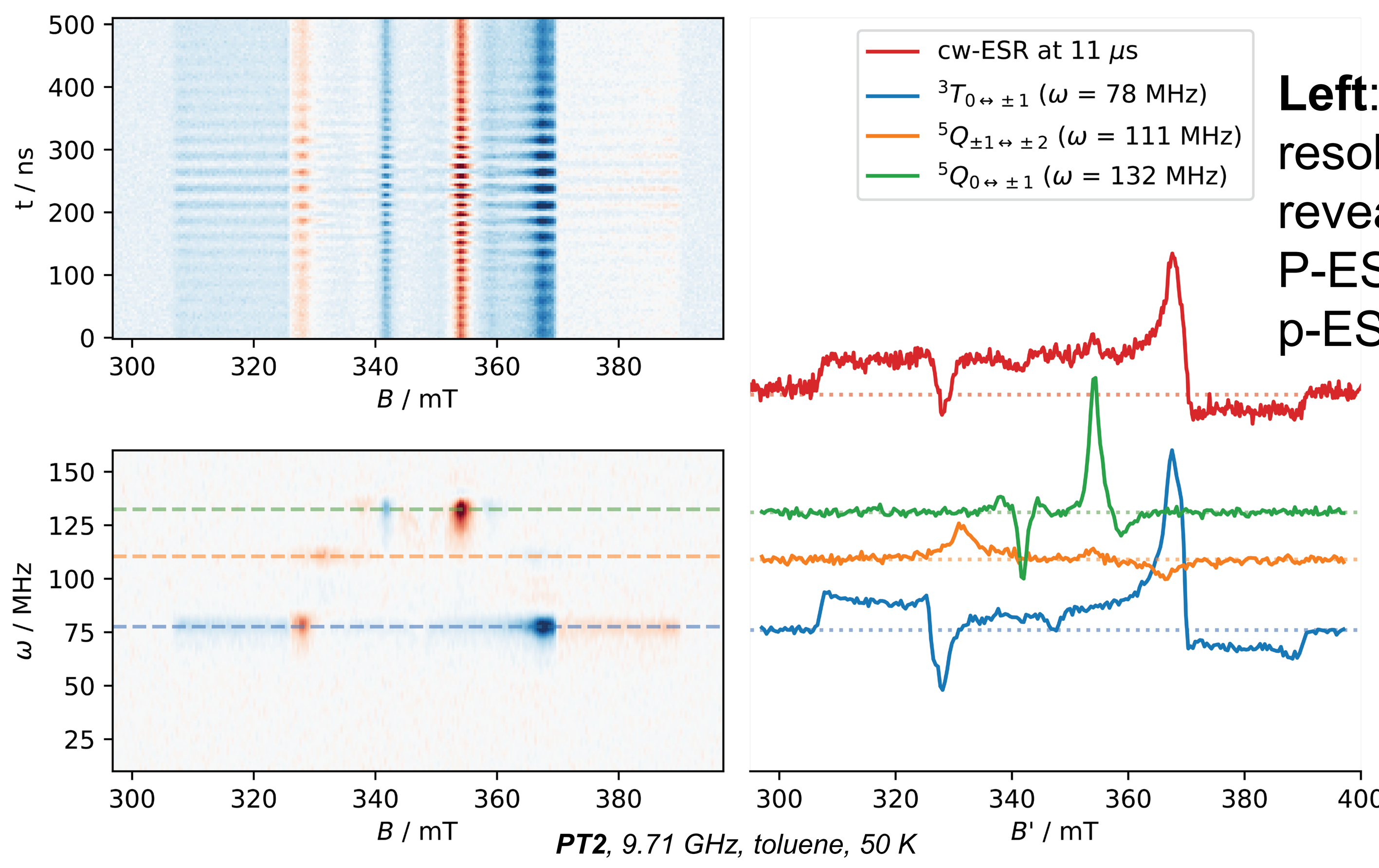
PT2 dimer used for all ESR studies

Transient cw-ESR reveals evolving spin populations

- Narrow ^{5}(TT)$_{0\leftrightarrow\pm1}$ transitions within <100 ns
- Broader ^{3}T$_{0\leftrightarrow\pm1}$ transitions 1 – 10s of μs
- Mainly m_s=0, net absorptive: more m_s<0 than m_s>0
- Assigned by fitting, analogy: cw-ESR information poor
- Overlapping signals complicate analysis

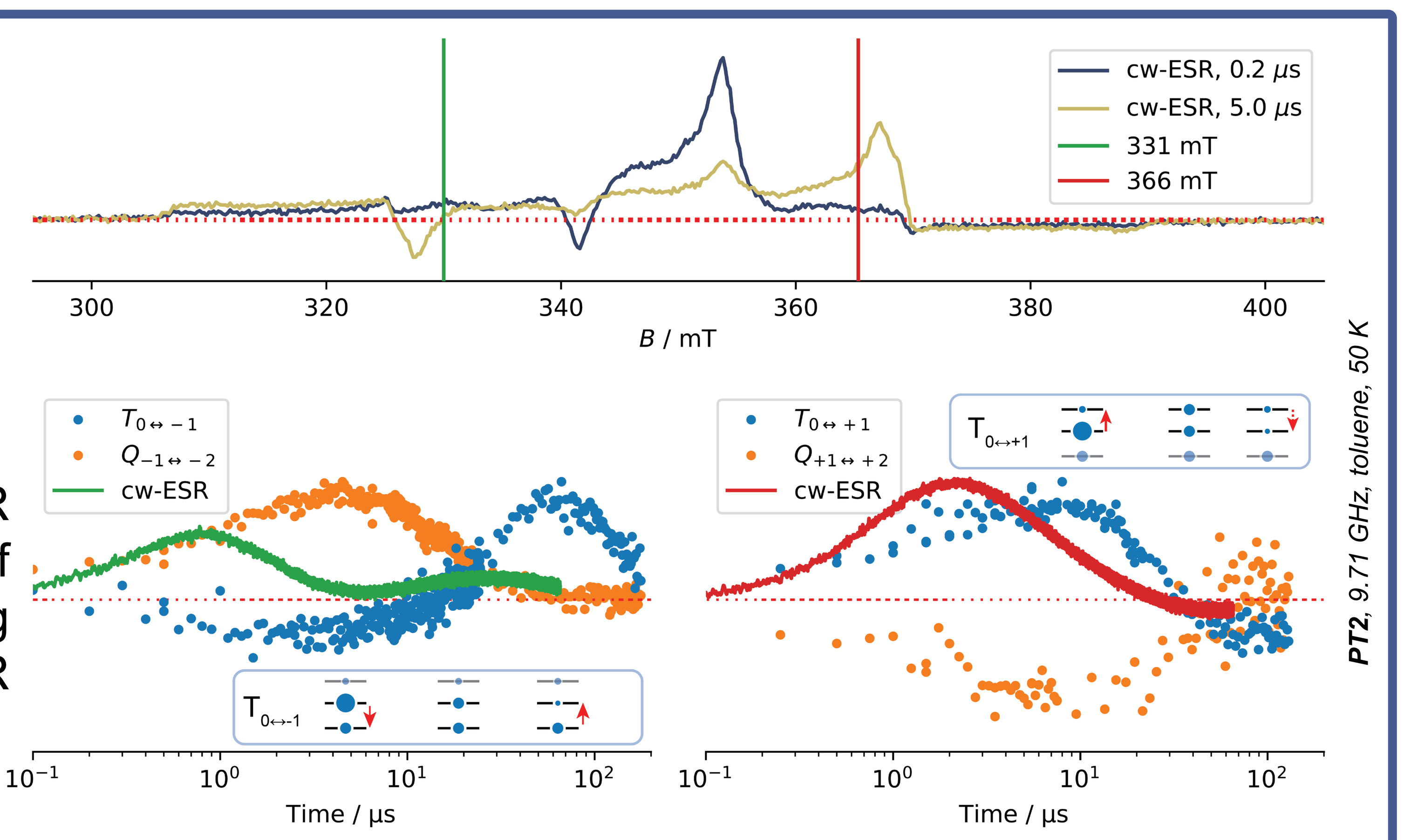
Resolving transitions with nutation p-ESR

SF cw-ESR spectra are **complex and overlapping**. Nutation p-ESR lets us **identify** (1D) or **resolve** (2D) transitions by field or time.



Left: 2D field-swept PEANUT p-ESR resolves signals by S and $|m_s|$, revealing surprise $m_s = \pm2$ quintets. P-ESR quintets seem less absorptive p-ESR triplets (or cw-ESR)

Right: 2D time-swept p-ESR nutation resolves dynamics of overlapping transitions, finding slower kinetics than cw-ESR

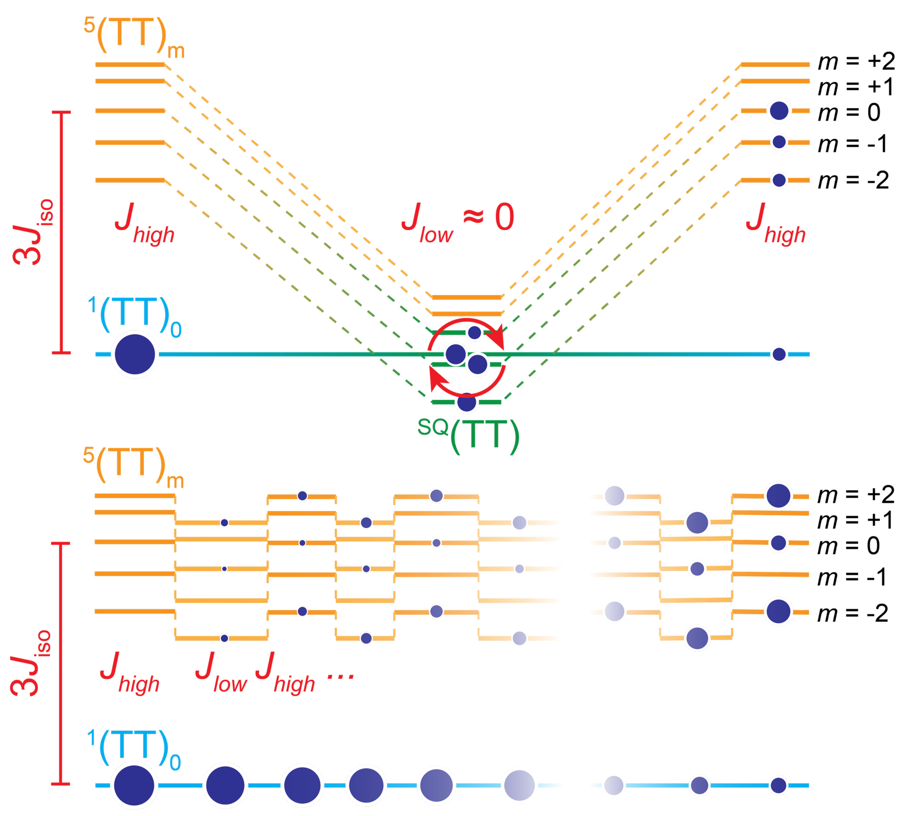


Quintets form with dynamic J_{iso}

Narrow (D-3E)/3 quintet spectra are only possible when inter-triplet J_{iso} is large, but large J_{iso} prevents ^{1}(TT)$_0\leftrightarrow$ ^{5}(TT)$_m$ mixing: suggests a **time-dependent** J_{iso}. In a two-triplet basis:

$$\hat{H}_{spin} = \hat{H}_{ee}(t) + \hat{H}_{zee} + \hat{H}_{zfs}$$
$$= J_{iso}(t)\hat{S}_1\cdot\hat{S}_2 + \sum_{i=1,2}\mu_B g \mathbf{B_0}\cdot\hat{S}_i + \hat{S}_i\cdot\mathbf{D}_i\cdot\hat{S}_i$$

We simulate ^{5}(TT)$_m$ formation by solving the TD Schrödinger for a modelled time-dependent Hamiltonian[2] and find **two distinct modes** of ^{1}(TT)$_0\leftrightarrow$^{5}(TT)$_m$ mixing, depending on whether $J(t)$ is ever 'small'.

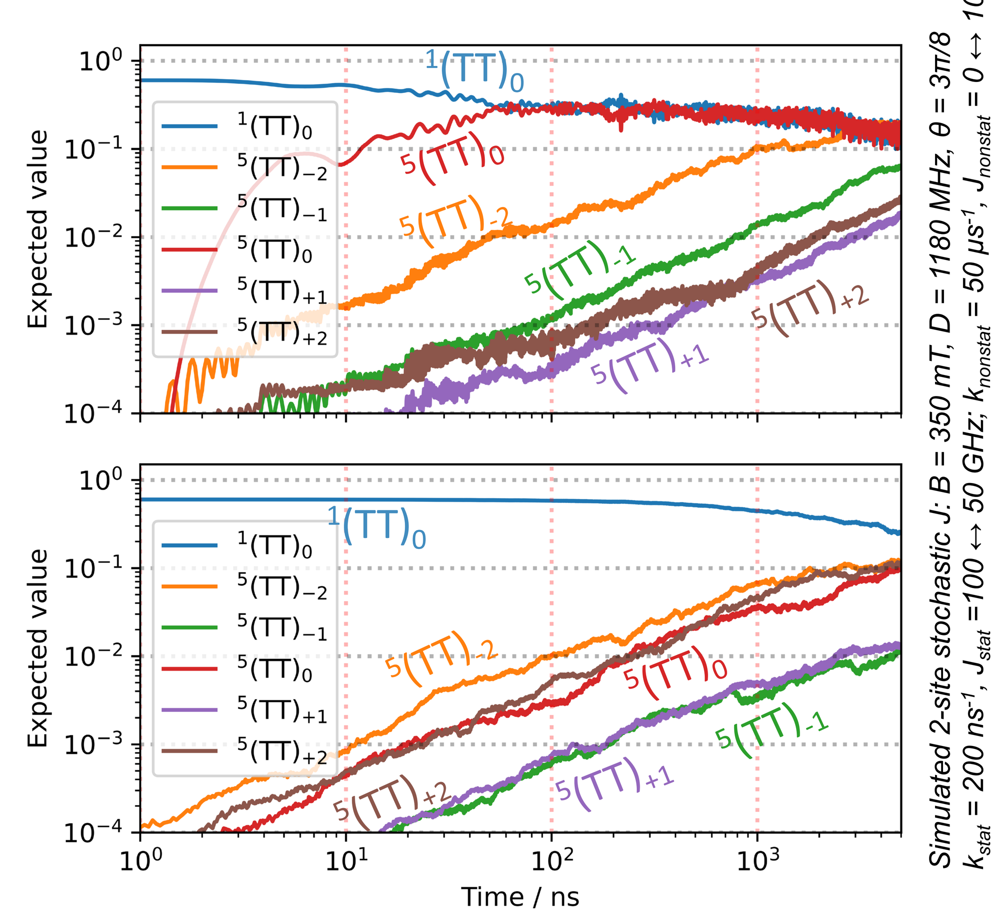


'Non-stationary' quintets

- Fast mixing at low J
- Biases m_s<0 if adiabatic
- Dynamic $J(t)$ follows slow, larger-scale motions?
- Short coherence times?

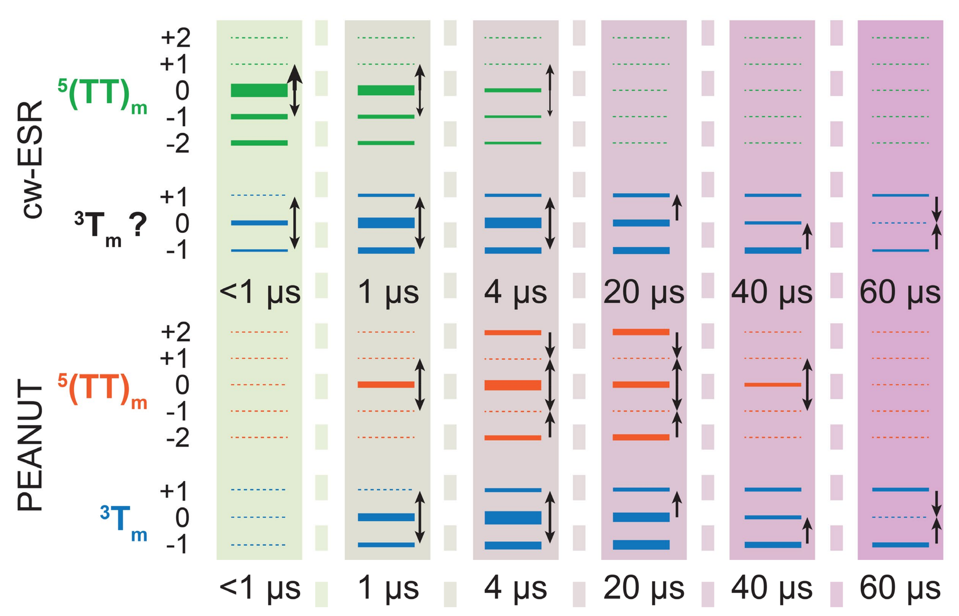
'Stationary' quintets:

- Slow mixing while $J(t)$≫0
- Diabatic; $|m_s|$-dependent
- Dynamic $J(t)$ follows fast, smaller-scale motions?
- Long coherence times?



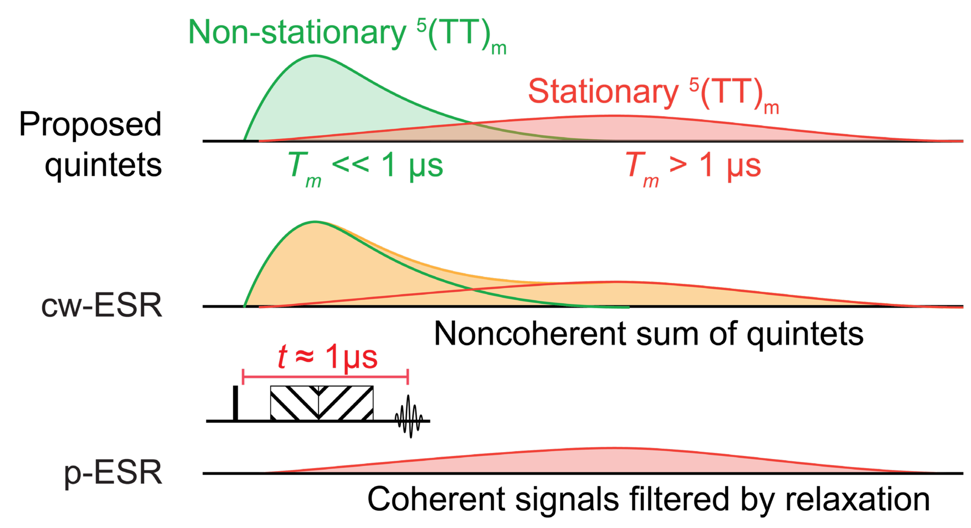
Conclusions: how to reconcile cw-ESR & p-ESR?

- Cw-ESR signals are prompt, net-absorptive; consistent with 'non-stationary' formation
- P-ESR signals are delayed, comparable ±m_s character; consistent with 'stationary' formation



Populations, dynamics consistent with coexisting quintet pathways

- Non-stationary prompt quintets relax quickly → filtered out of p-ESR
- How does a slow process compete with a fast one? Not yet clear…



References

[1]Tayebjee, M. J. Y. *et al. Nature Physics* **13**, 182–188 (2017).
[2]Collins, M. I., et al. *J. Chem. Phys.* **151**, 164104 (2019).

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Australian Government Australian Research Council

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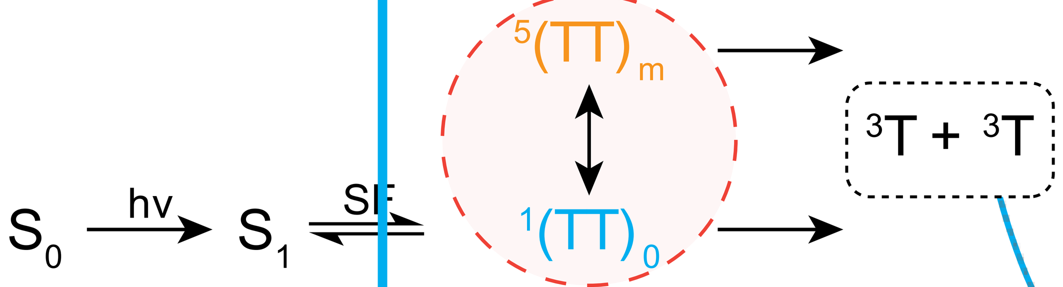
Singlet fission in molecular dimers

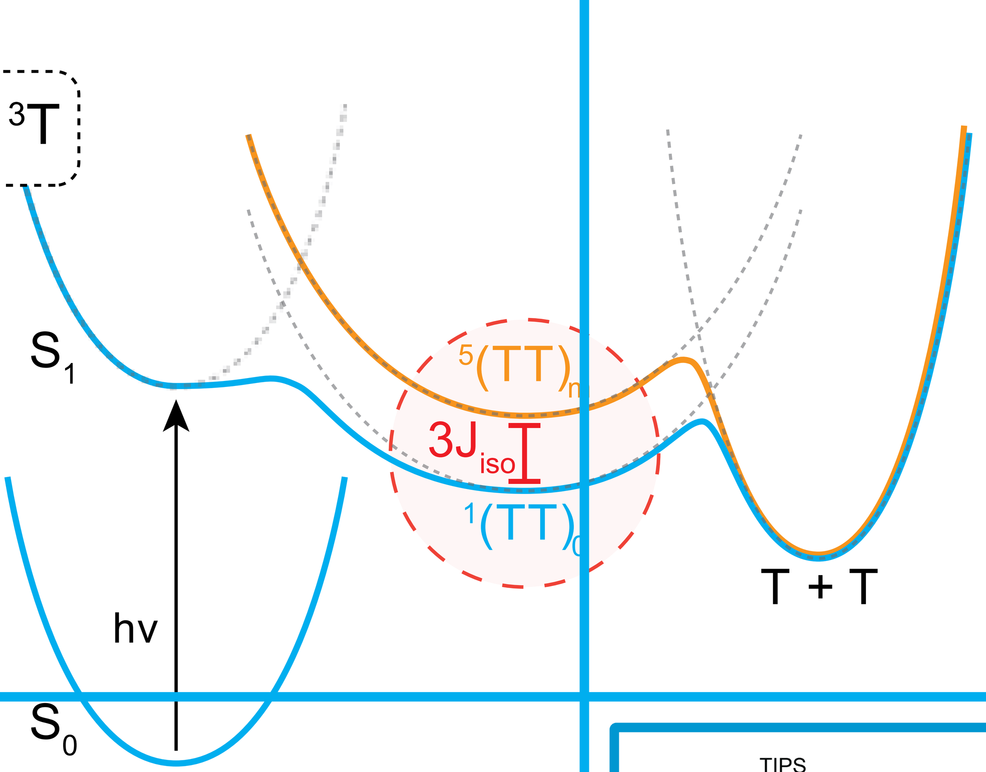


Singlet fission (SF): decay of a singlet exciton into coupled triplet pair (TT)

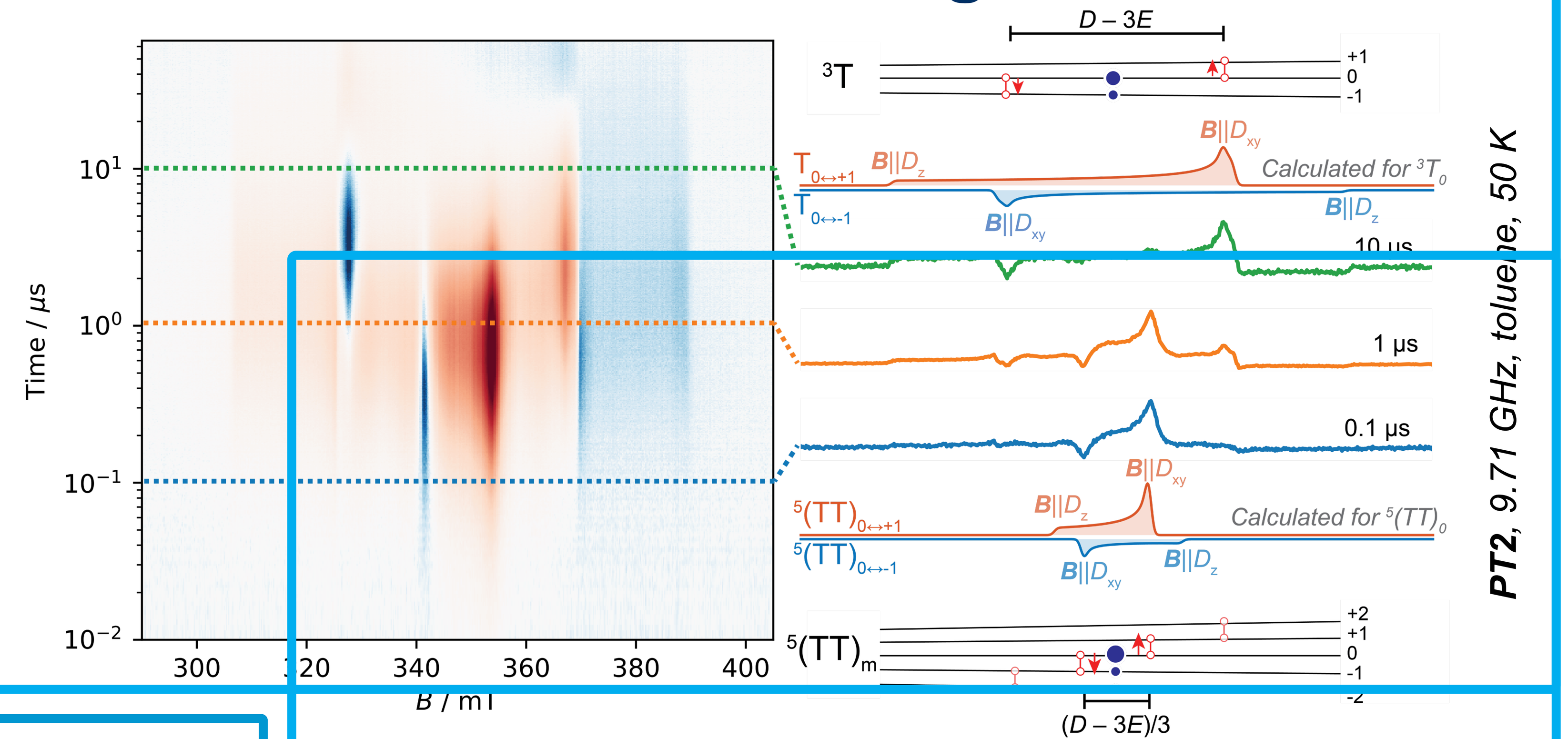
- Initial singlet ^{1}**(TT)$_0$**, can dephase to $^{S(S+1)}$**(TT)$_m$** or dissociate to free triplets

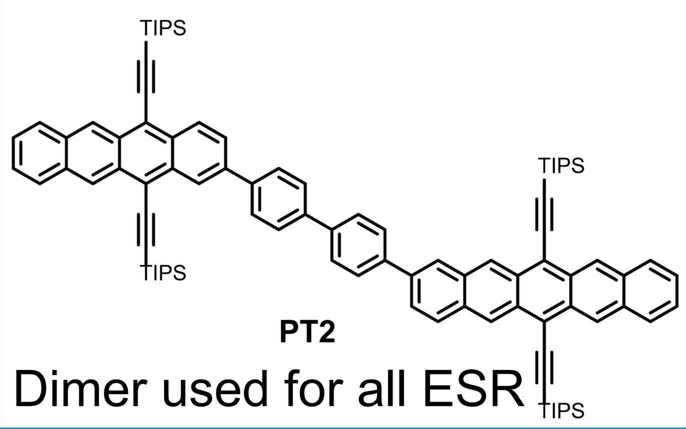
We care about SF because:

- Downconversion improves photovoltaics
- Well-defined spin states may be useful for quantum information or photo-DNP.



Transient cw-ESR of singlet fission





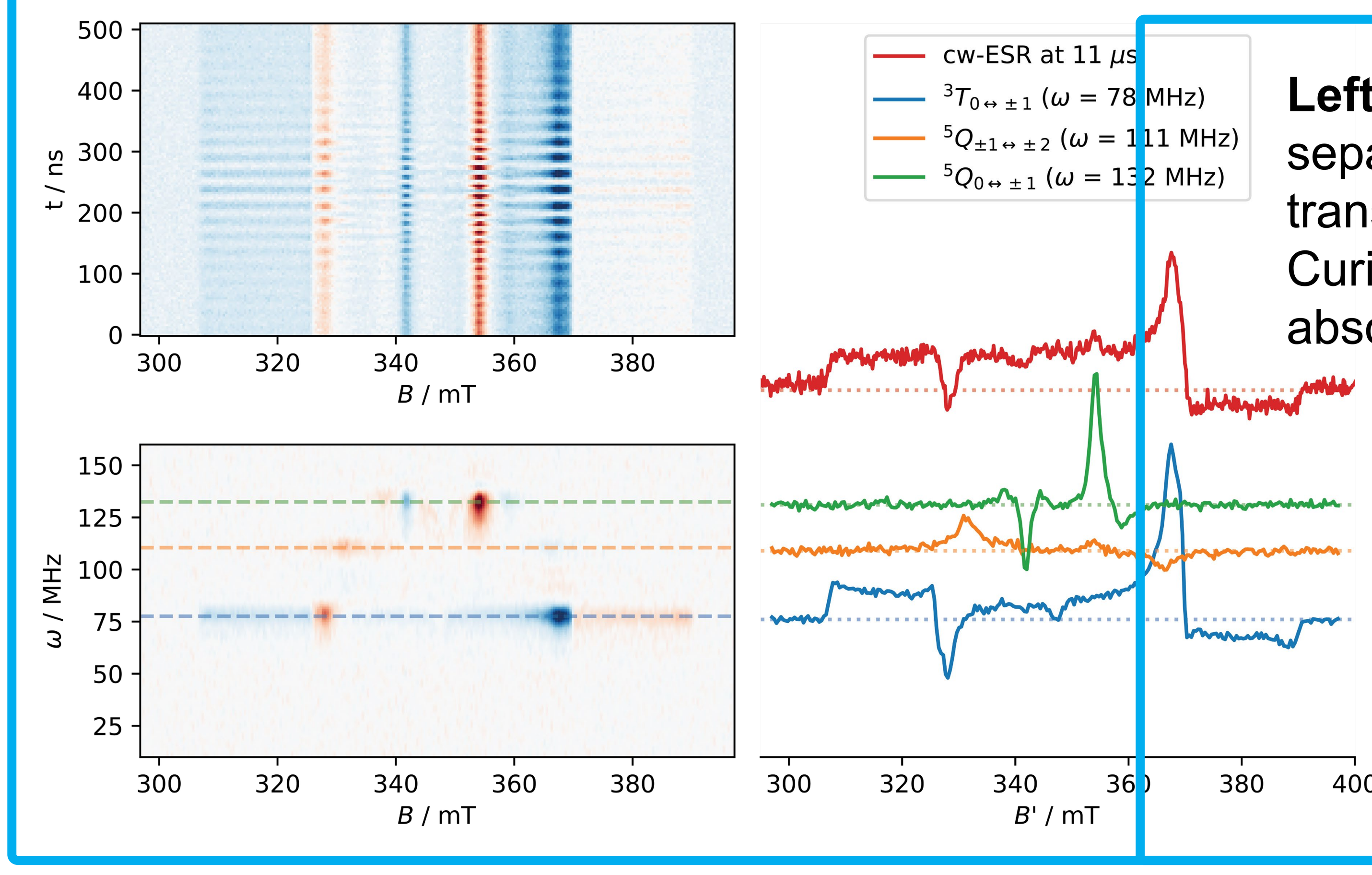
Dimer used for all ESR

High-spin states in SF evolve over µs – **can use tr-ESR to study excited state spin dynamics**. Here:

- Narrow ^{5}(TT)$_0$ signals form < 100 ns
- Then, broader ^{3}T signals.
- Spins mainly m_s=0, with more m_s<0 than m_s>0

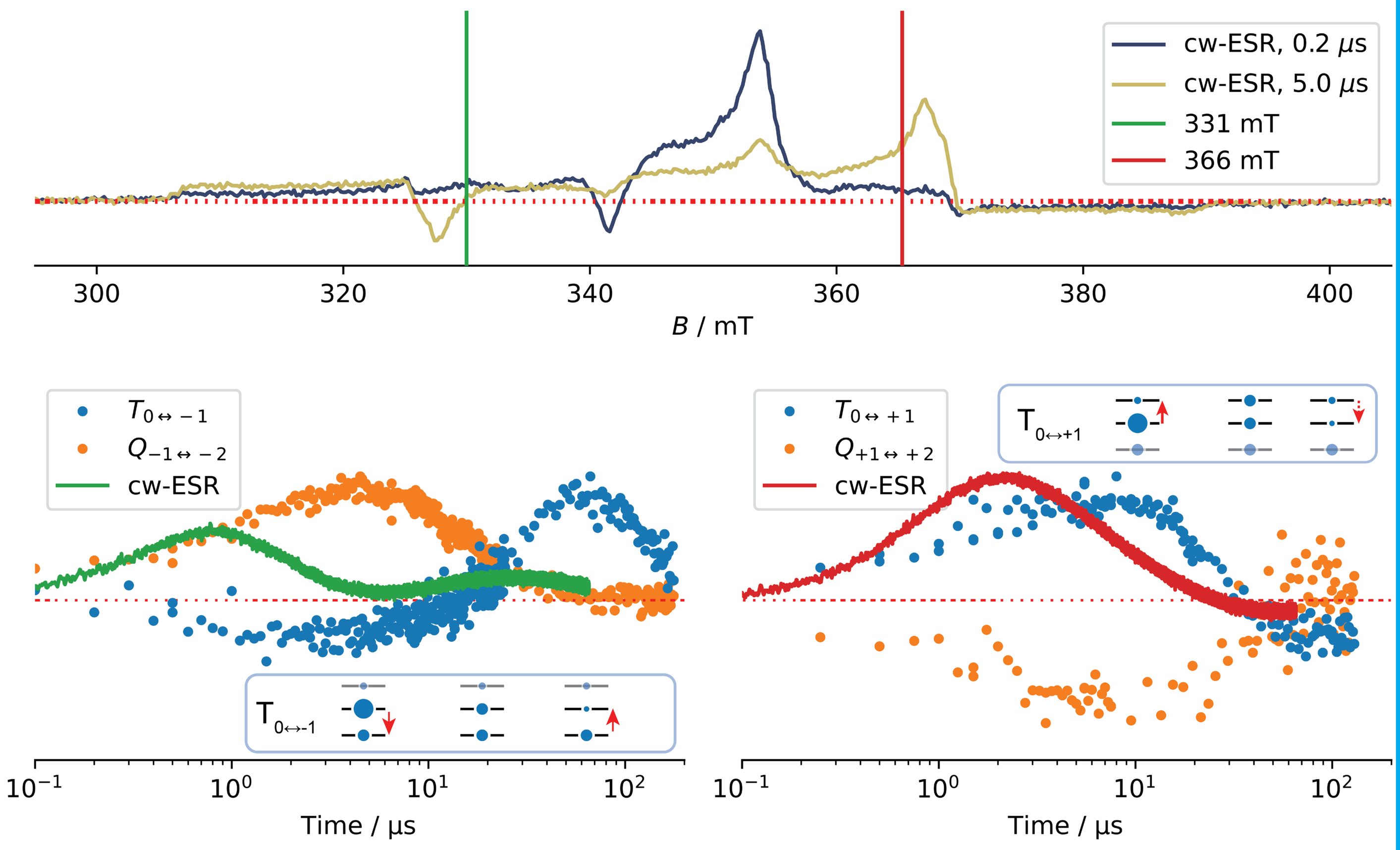
Resolving transitions with nutation p-ESR

SF forms a complex mixture of overlapping ESR signals, and transient cw-ESR can't identify the transitions involved.
We use nutation p-ESR to resolve transitions over ***B*** field or time.



Left: field-swept 2D PEANUT nutation separates triplet and quintet transitions, revealing ^{5}(TT)$_{\pm2}$ quintets. Curiously, the ^{5}(TT) quintets are less absorptive than the ^{3}T triplets

Right: *time*-swept 2D nutation resolves overlapping transition dynamics and ^{3}T population inversion. The p-ESR signals rise and fall more slowly than cw-ESR signals at the same fields.



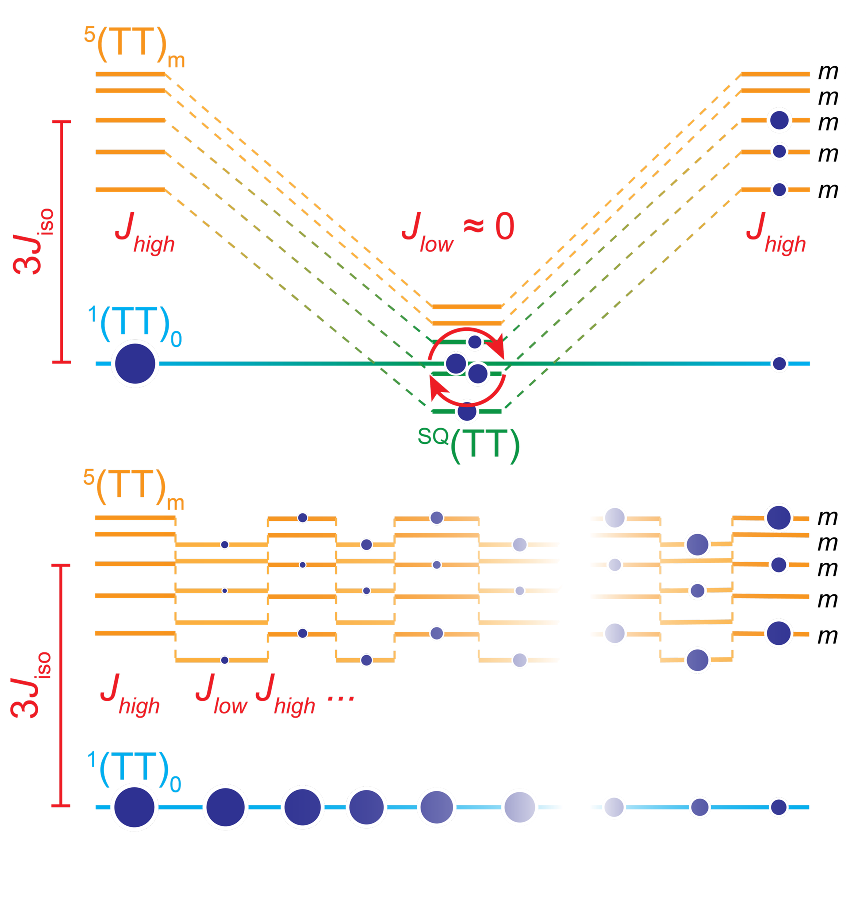
Quintet formation requires dynamic J_{iso}

- $\hat{H}_{ZFS}$ only mixes ^{1}(TT)$_0$ with ^{5}(TT)$_m$ when spin-spin term $\hat{H}_{ee}$ is small – but narrow quintet ESR spectra require large $\hat{H}_{ee}$!
- Solve with a time-dependent $\hat{H}_{ee}$. In the two-triplet basis:

$$\hat{H}_{spin} = \hat{H}_{ee} + \hat{H}_{zee} + \hat{H}_{zfs}$$

$$= J_{iso}(t)\widehat{S_1}\cdot\widehat{S_2} + \sum_{i=1,2}\mu_B g \boldsymbol{B_0}\cdot\widehat{\boldsymbol{S}}_i + \widehat{\boldsymbol{S}}_i\cdot\boldsymbol{D}_i\cdot\widehat{\boldsymbol{S}}_i$$

- Simulate quintet formation by solving the time-dependent hamiltonian[2] with a model *J(t)* term
  - Model? Site hopping, molecular dynamics, open quantum systems… Stay tuned!
- We see **two distinct pathways** to quintet formation, depending on whether *J(t)* is ever 'small'

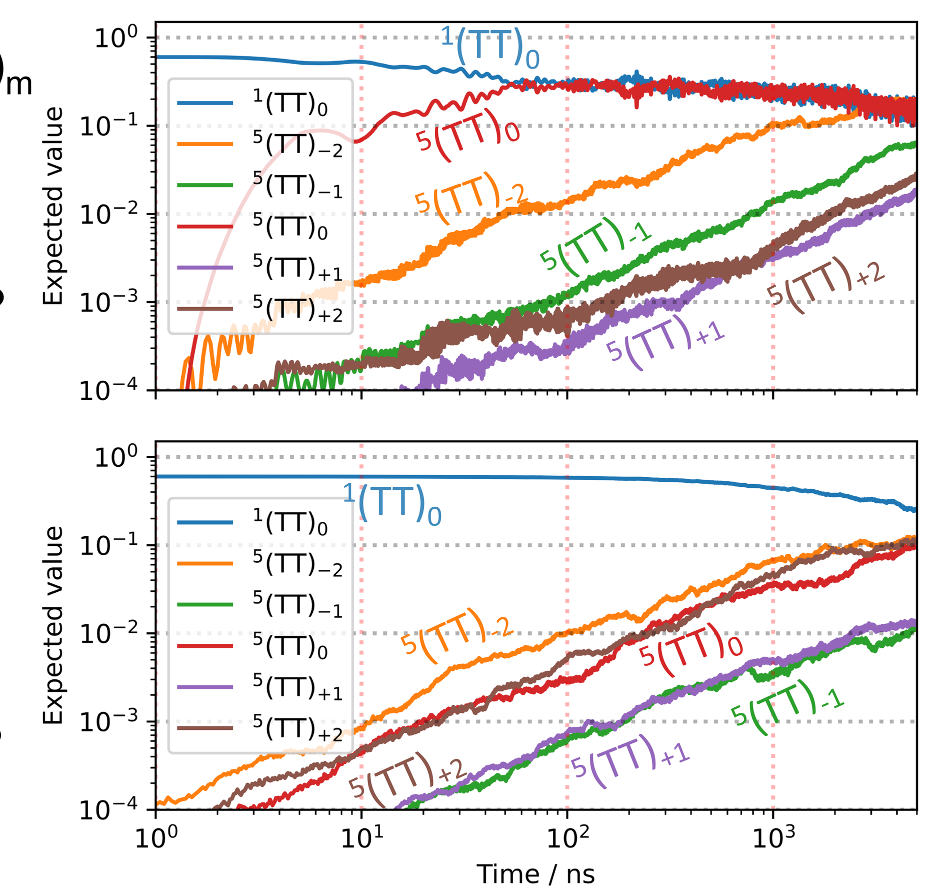


'Non-stationary' ^{1}(TT)$_0$↔^{5}(TT)$_m$

- Fast mixing at low *J*
- Limited coherence times?
- Adiabatic transit →^{5}(TT)$_{m<0}$
- Slow, large-scale dynamics?

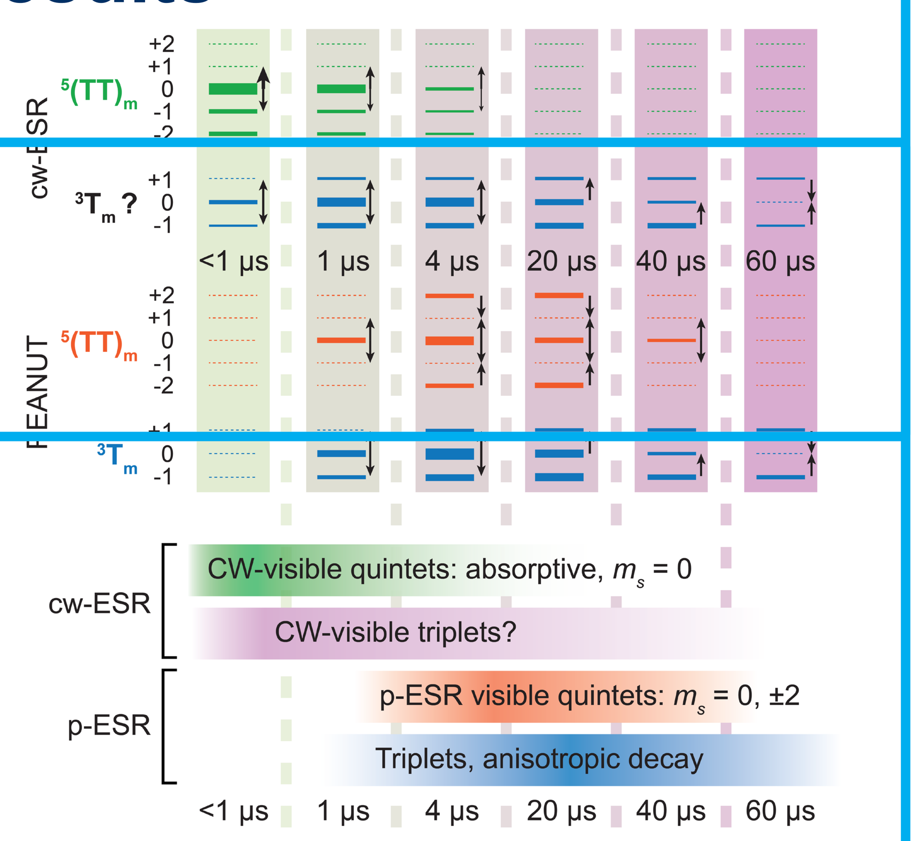
'Stationary' ^{1}(TT)$_0$↔^{5}(TT)$_m$

- Slower mixing while *J(t)*≫0
- Longer coherence times?
- Diabatic transfer →^{5}(TT)$_{\pm2}$
- Fast, small-scale dynamics?



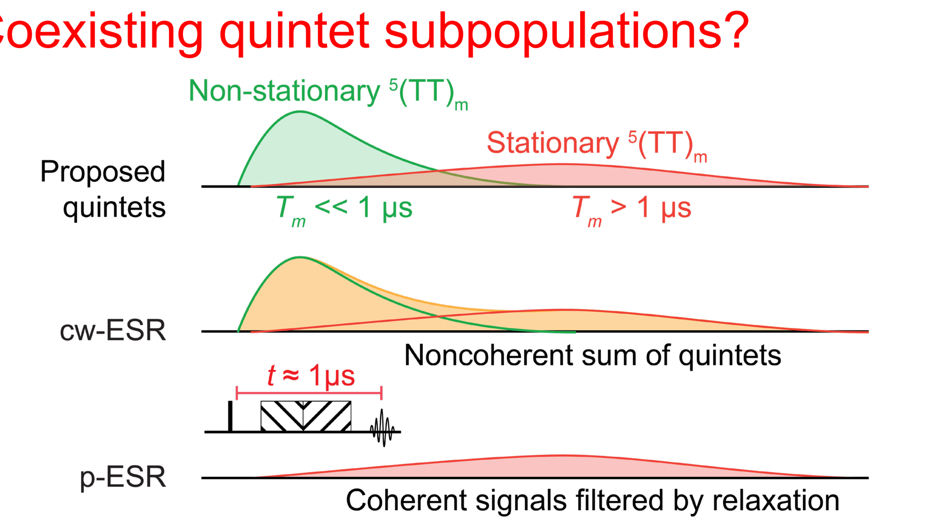
Reconciling cw-ESR and p-ESR results

We see different populations and dynamics by cw-ESR and p-ESR. *J(t)* reaches zero. Fast coherent mixing, possibly limited spin coherence times, adiabatic transit back to J_{high} biases toward low-lying quintets



- Prompt quintets consistent with non-stationary formation
- Delayed p-ESR visible quintets look stationary

Coexisting quintet subpopulations?



For Further Information

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References

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