Australian Research Council Centre of Excellence in exciton science

# Spin Dynamics in Singlet Fission

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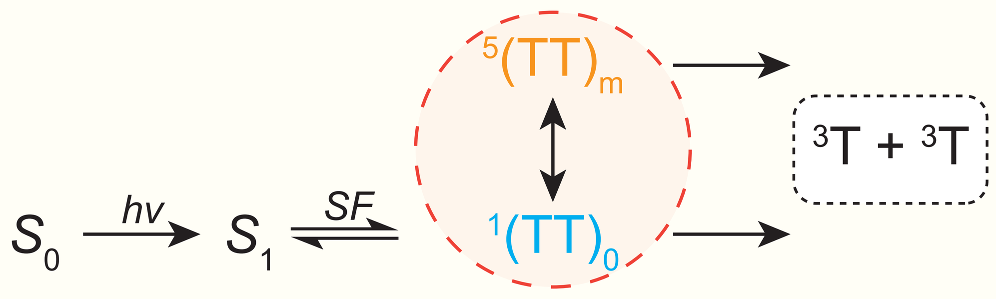
## Singlet fission in molecular dimers

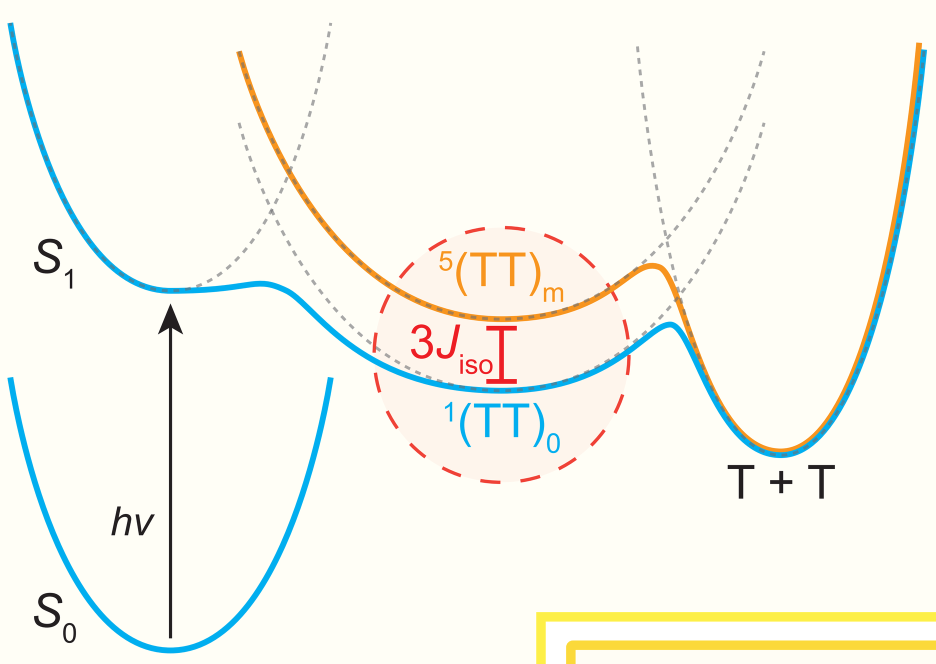



**Singlet fission**: the transition from one singlet exciton to coupled triplet pair $^1(TT)_0$

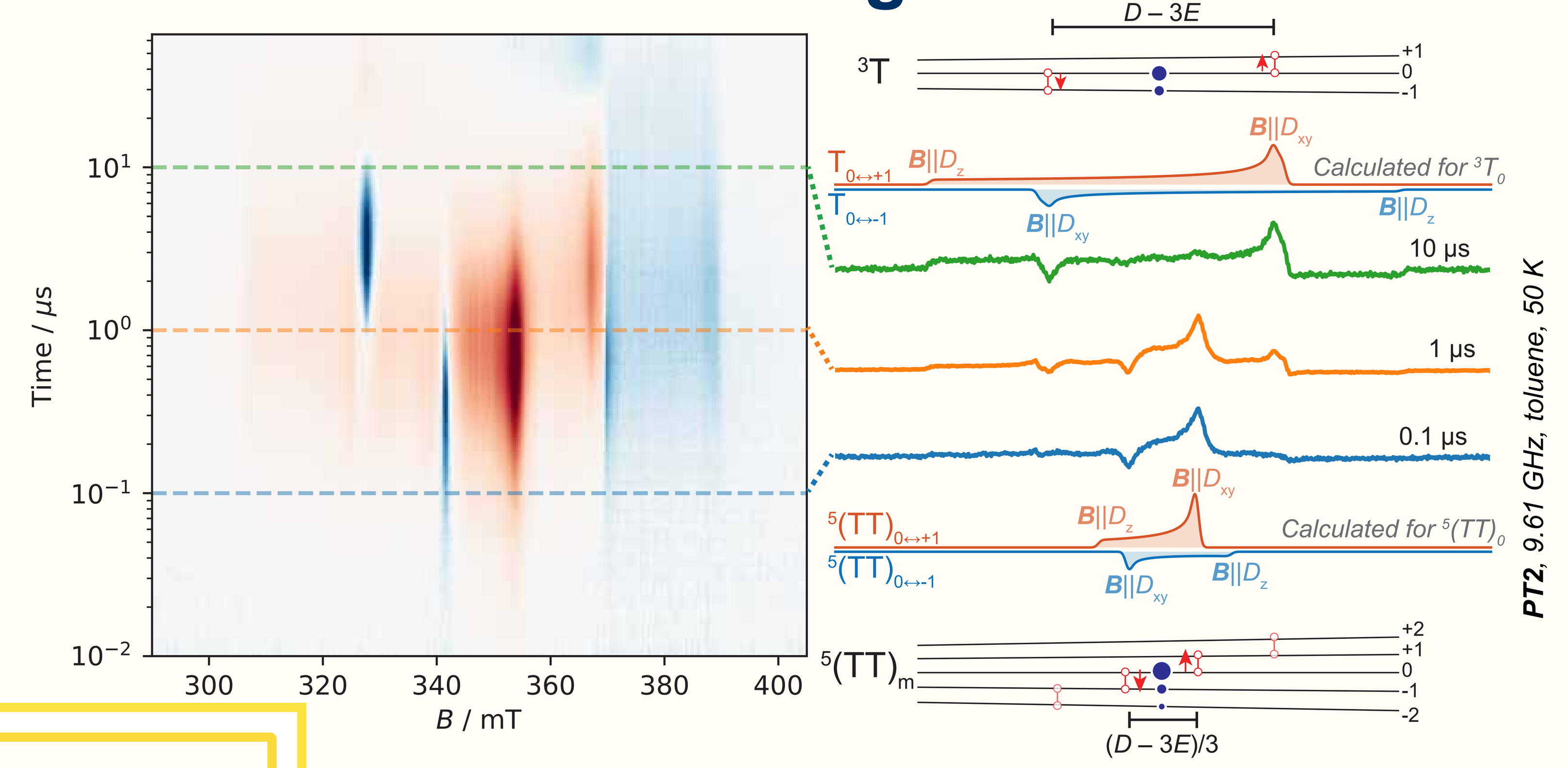
- $^1(TT)_0$ can **dephase**[1] to $^{S(S+1)}(TT)_m$
- $^n(TT)_m$ can **dissociate** to free triplets

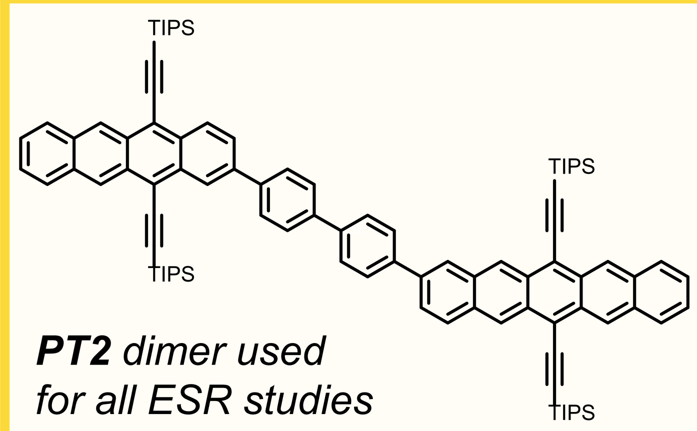
Opportunities:

- Downconversion for better photovoltaics
- Photogenerated spin states for quantum information,[2] DNP[3]




## Transient cw-ESR of singlet fission



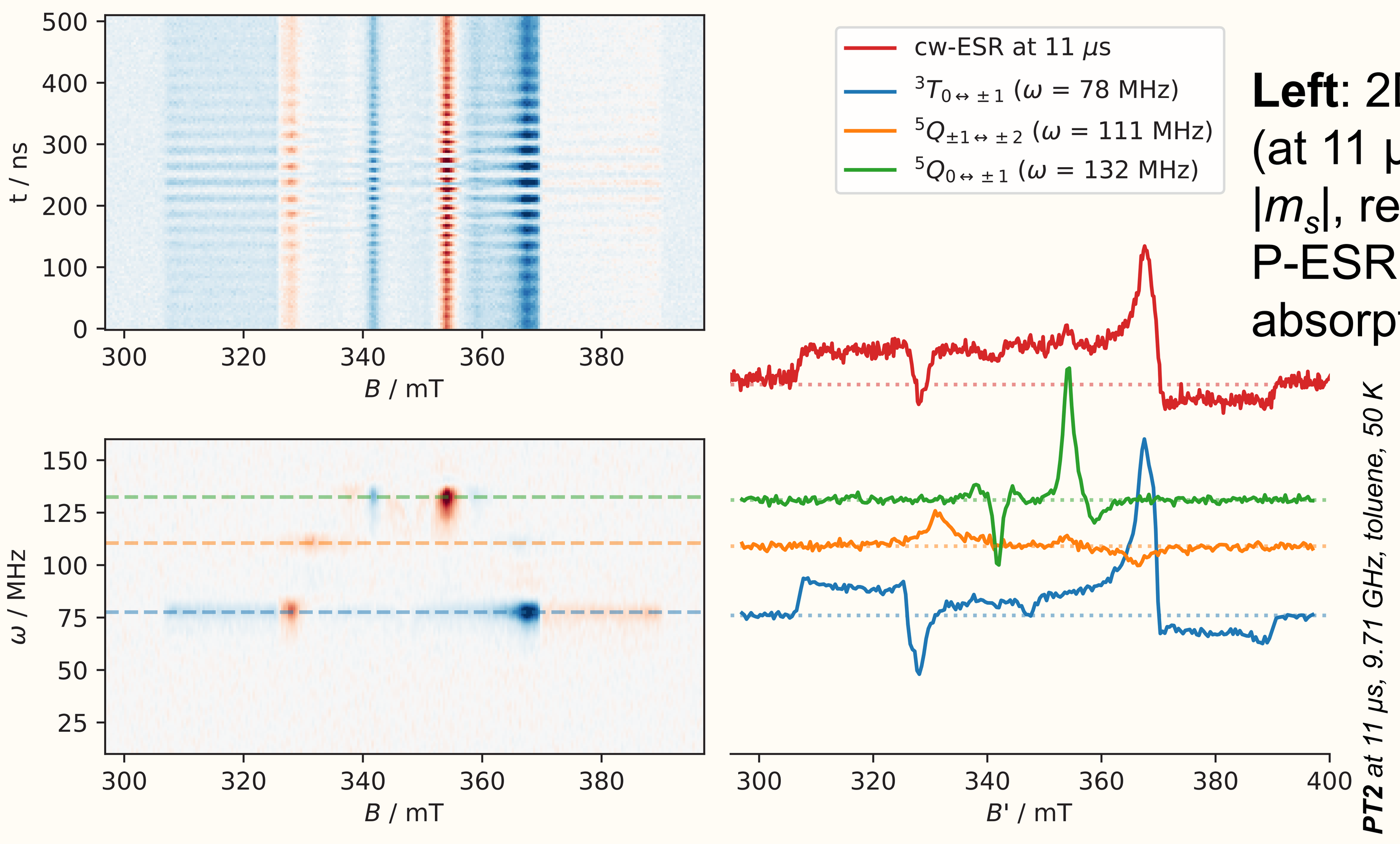

*PT2 dimer used for all ESR studies*

**Transient cw-ESR reveals evolving spin populations**

- Narrow $^5(TT)_{0\leftrightarrow\pm1}$ signals from <100 – 1000s of ns
- Broader $^3T_{0\leftrightarrow\pm1}$ signals from 1 – 10s of µs
- Mainly $m_s = 0$, **net absorptive**: more $m_s$<0 than $m_s$>0
- Transitions assigned by fitting, analogy; analysis complicated by spectral overlap

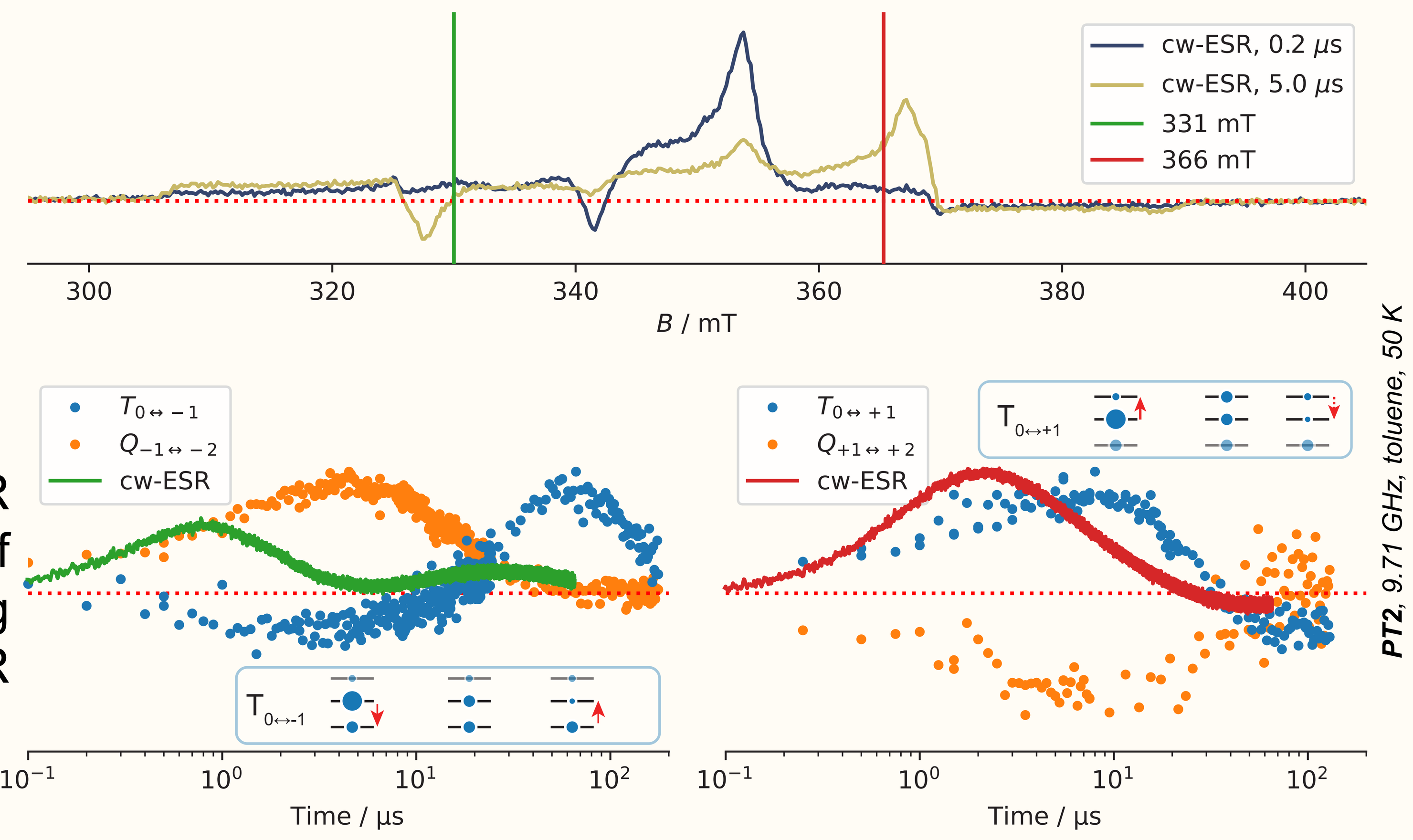
## Resolving transitions with nutation p-ESR

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[4] p-ESR (at 11 µs) resolves signals by $S$ and $|m_s|$, revealing $m_s = \pm2$ quintets. P-ESR quintet signals seem less absorptive than triplets, or cw-ESR

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



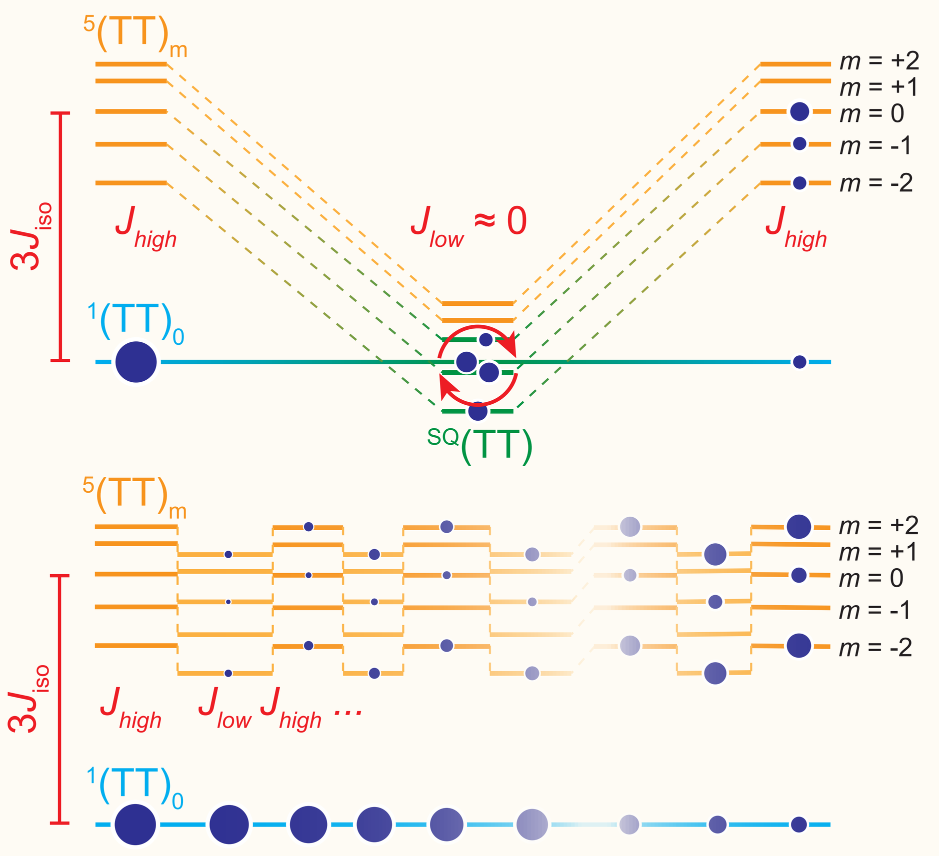

## Quintets form with dynamic $J_{iso}$

Narrow quintet ESR spectra only possible when inter-triplet coupling $J_{iso}$ is large, but that prevents $^1(TT)_0 \leftrightarrow {^5(TT)_m}$ mixing: we need a **time-dependent** $J_{iso}(t)$. In a two-triplet basis:

$$\hat{H}_{spin} = \hat{H}_{ee}(t) + \hat{H}_{zee,i} + \hat{H}_{zfs,i}$$

$$= J_{iso}(t)\left(\hat{S}_1 \cdot \hat{S}_2\right) + \sum_{i=1,2}\left(\mu_B g \boldsymbol{B_0} \cdot \hat{S}_i + \hat{S}_i \cdot \boldsymbol{D}_i \cdot \hat{S}_i\right)$$

We simulate $^5(TT)_m$ formation by solving the TD Schrödinger equation for $^1(TT)_0$ evolving under a model spin Hamiltonian[5,6] to find **two distinct modes** of $^1(TT)_0 \leftrightarrow {^5(TT)_m}$ mixing, depending on whether $J_{iso}(t)$ is ever 'small'.

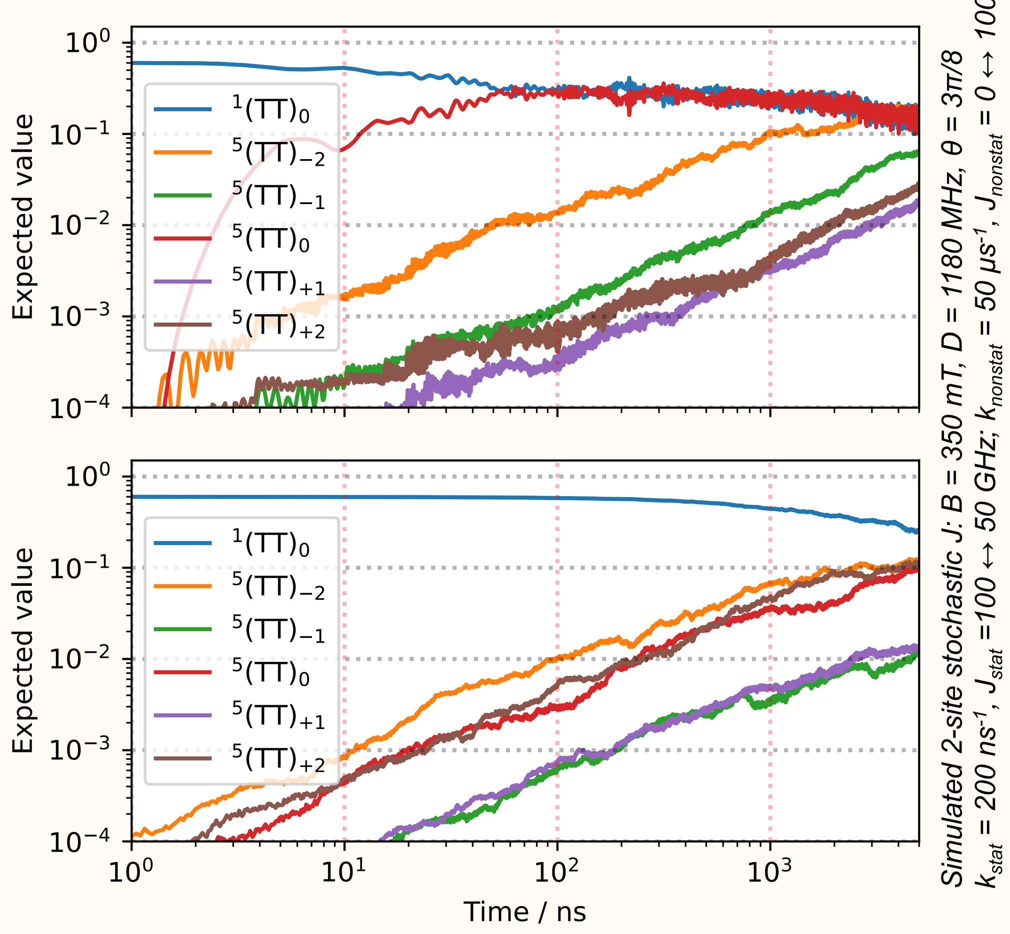



**'Non-stationary' quintets**[5]

- $J_{iso}(t)$ sometimes small: fast coherent mixing
- Biases $m_s$<0 if adiabatic
- Results from slow, large molecular dynamics?
- Short coherence times?

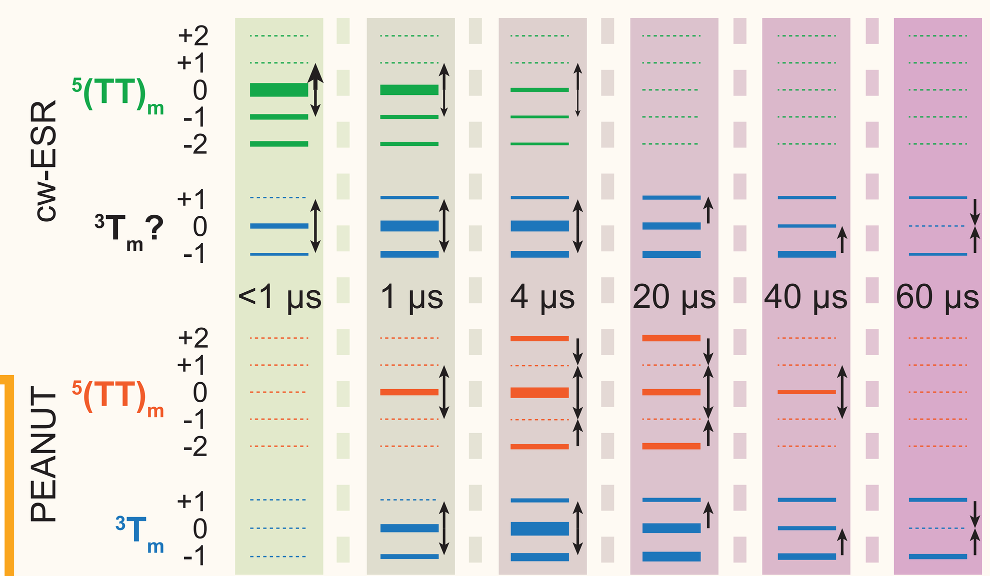
**'Stationary' quintets**[6]

- $J_{iso}(t)$ never small, jumps: slow diabatic transitions
- Comparable rates for $\pm m_s$
- Results from fast, small molecular dynamics?
- Long coherence times?



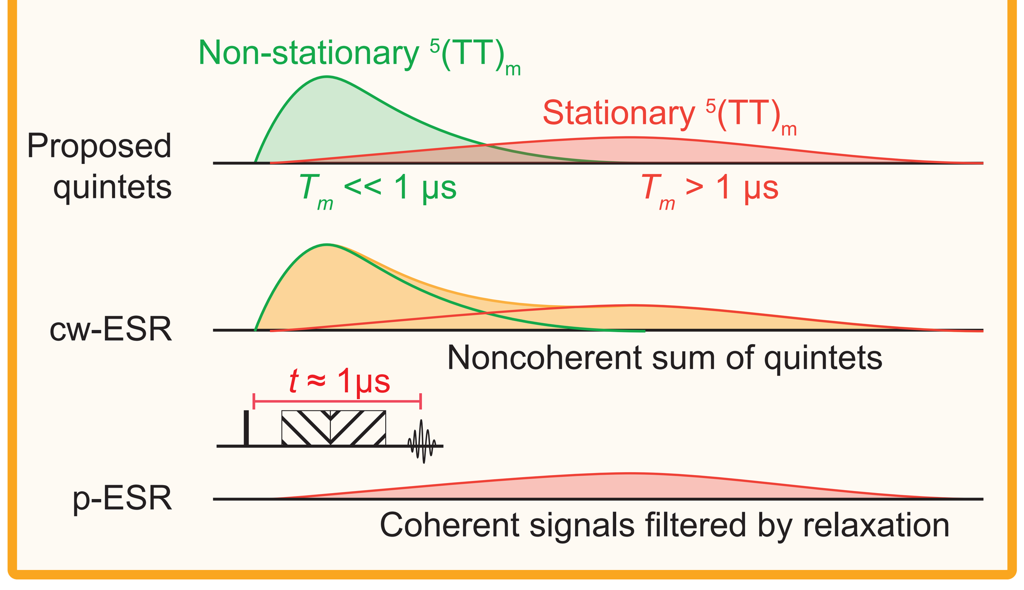

## Conclusions: cw-ESR, p-ESR, and theory

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




**Populations, dynamics consistent with coexisting quintet pathways**

- Non-stationary prompt quintets relax quickly: filtered out of p-ESR
- What are the physical mechanisms, and why the mix? Good questions…




**References**

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