

# Signatures of chirality-induced spin selectivity in time-resolved EPR of light-induced radical pairs

Robert Bittl<sup>1</sup>, Mario Chizzini<sup>2</sup>, Emilio Macaluso<sup>2</sup>, Alessandro Chiesa<sup>2</sup>, Roberta Sessoli<sup>3</sup>, Stefano Carretta<sup>2</sup>

<sup>1</sup>Berlin Joint EPR Lab, Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

<sup>2</sup>Dipartimento di Scienze Matematiche, Fisiche e Informatiche, Università di Parma, I-43124 Parma, Italy; INFN-Sezione di Milano-Bicocca, gruppo collegato di Parma, 43124 Parma, Italy; UdR Parma, INSTM, 43124 Parma, Italy

<sup>3</sup>Dipartimento di Chimica "Ugo Schiff" & INSTM, Università Degli Studi di Firenze, 50019 Sesto Fiorentino, Italy

## Introduction

Chirality-induced spin selectivity (CISS), a phenomenon observed for charge transport through chiral media, has recently gained high interest due to resulting large spin polarization even at room temperature. The effect has been documented in a wide variety of samples [1]. Even for light-induced electron transport through photosystem I strongly spin-polarized current has been reported [2]. Irrespective of the huge experimental body of work, a thorough theoretical understanding of the effect is still lacking and object of intense debate. In order to gain insight into the mechanism underlying the CISS phenomenon, we investigate by time-resolved EPR light-induced electron transfer in the well-studied photosynthetic reaction centers as well as molecular donor-chiral linker-acceptor dyads (D- $\chi$ -A) and triads (D- $\chi$ -A-Q) with a stable paramagnetic species Q acting as a sensor of the local A polarization. Initially, we focus on the theoretical requirements for detecting CISS signatures in transient EPR (trEPR) as well in the spectral as in the time domain and pulsed EPR (out-of-phase (OOP)-ESEEM).

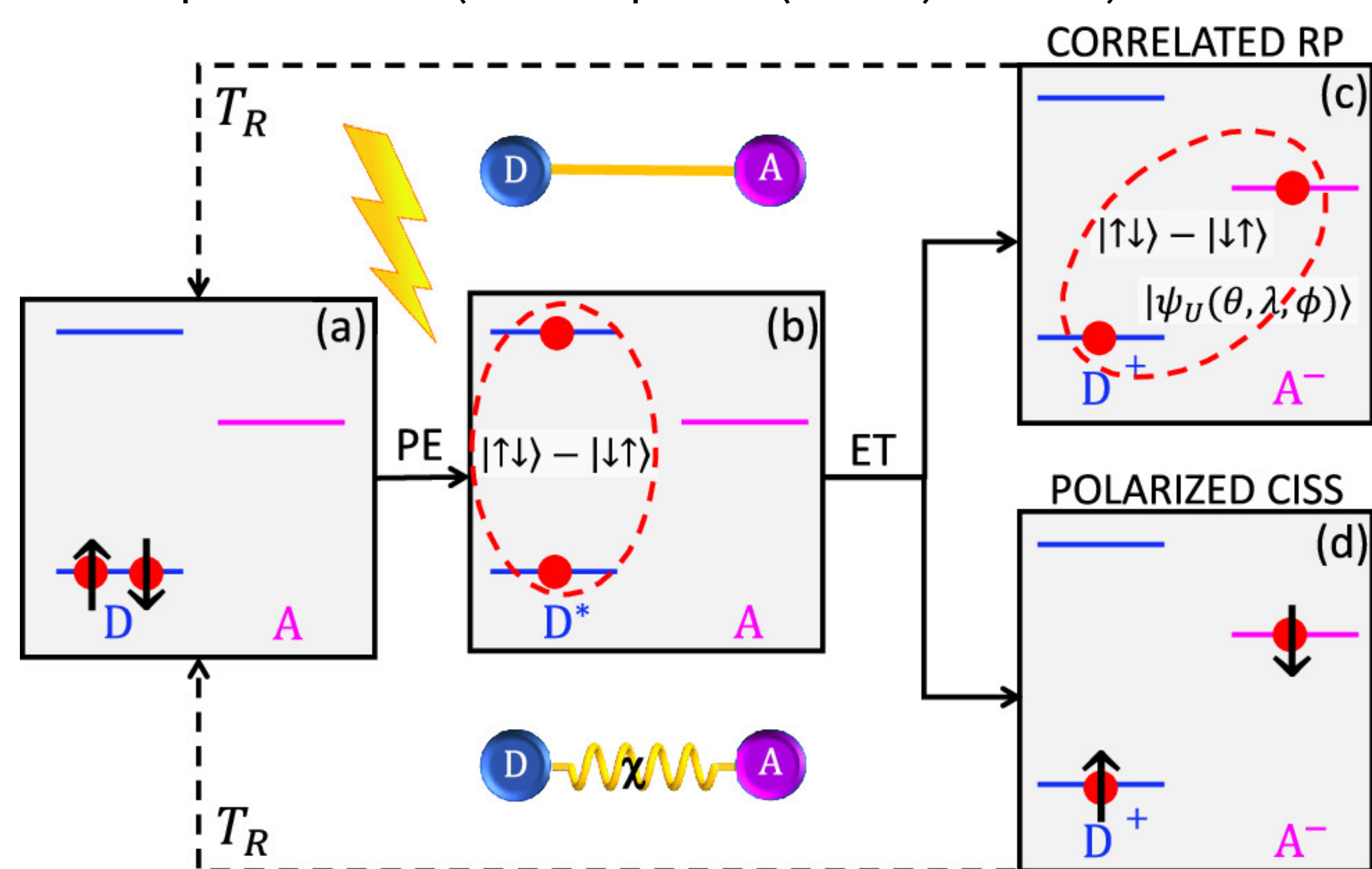


Figure 1. Scheme of the electron-transfer mechanism: (a) singlet initial state on the donor D (with two electrons both in the ground orbital). Photoexcitation (PE) brings it to the D\*A singlet state in which one electron is excited (b), but the pair is still in an entangled state (dashed circle). After electron transfer (ET) of the excited electron to the acceptor (A), the final state is still either a correlated radical pair (RP, c) or a polarized state after transfer through a chiral bridge (d). Recombination to the initial singlet (or to the triplet) state occurs on a time scale  $T_R$  (dashed arrows). Top (bottom) inset: Scheme of the DA radical pair, linked by a linear (chiral) bridge. (Figure from [3])

## The model

We use the static high-field rotating frame Hamiltonian in angular frequency units for the spin pair as

$$H_0 = \Omega_S(S_{za} + S_{zb}) + q(S_{za} - S_{zb}) + (d - J)S_{za}S_{zb} - (d + J)(S_{xa}S_{xb} + S_{ya}S_{yb})$$

where  $\Omega_S = (g_a + g_b)\mu_B B_0/\hbar - \omega_{mw}$ ,  $q = (g_a - g_b)/2\mu_B B_0/\hbar$ , and  $d, J$  denote the (angle dependent) dipolar coupling and the isotropic exchange interaction, respectively.  $H_0$  and its derived Liouville superoperator including a driving microwave field and incoherent relaxation operators can be used to model trEPR spectra and time traces. For the description of OOP-ESEEM it is convenient to diagonalize  $H_0'$  by  $H_0' = UH_0U^{-1}$  with  $U = \exp(-i\xi(S_{xa}S_{xb} + S_{ya}S_{yb}))$  and  $\xi = \arctan[(d + J)/(2q)]$  [4].  $H_0'$  can then be expressed with  $q' = q \cos(\xi) - (d + J)/2 \sin(\xi)$  in its eigenbasis as

$$H_0' = \Omega_S(S_{za} + S_{zb}) + q'(S_{za} - S_{zb}) + (d - J)S_{za}S_{zb}$$

The different starting conditions for standard ET and CISS are represented by the respective density matrices, the isotropic  $\rho_{0,S} = 1/4 - (S_{xa}S_{xb} + S_{ya}S_{yb} + S_{za}S_{zb})$  and  $\rho_{0,C} = 1/4 + S_{\theta a} - S_{\theta b} - S_{\theta a}S_{\theta b}$  for an arbitrary electron transfer axis  $\theta$  with respect to  $B_0$ , coincident with the dipolar axis yielding  $d(\theta) = D(\cos^2\theta - 1/3)$ .

## Zero quantum coherences in trEPR

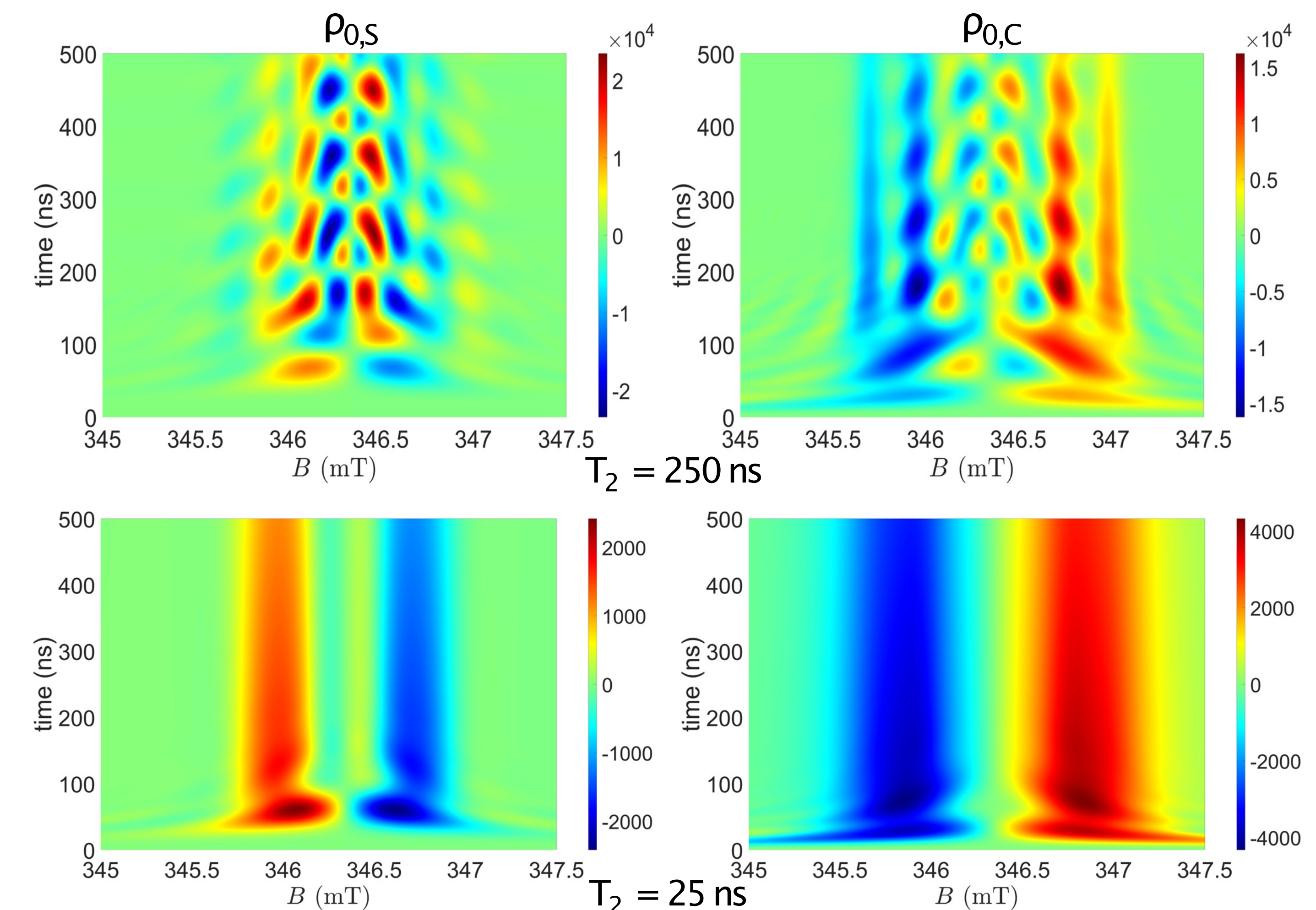


Figure 2. Time vs. magnetic field dependence of the in-phase transient signal  $S_V(t) = \text{tr}[(S_{ya} + S_{yb})\rho(t)]$  for  $g_a - g_b = 0.002$ ,  $\omega_{mw}/2\pi = 9.69$  GHz, and  $d$  corresponding to a D-A distance of 2 nm. The displayed signals are an ensemble average for randomly oriented D-A with respect to the magnetic field. At early times a clear difference in the signal rise is visible. This is due to the EPR blind initial state  $\rho_{0,S}$  without any magnetization yielding a quadratic signal rise with time while  $\rho_{0,C}$  contains single-spin polarization yielding linear signal rise. The difference is well visible for an assumed phase relaxation time  $T_2 = 250$  ns (upper panels) but is also clear even for a short  $T_2 = 25$  ns.

## OOP-ESEEM

The OOP-ESEEM signal intensity  $S_x(\tau) = \text{tr}[(S_{xa} + S_{xb})\rho(\tau)]$  characteristic for light-induced radical pairs shows a peculiar dependence on the flip angle  $\beta$  of the first pulse in a  $\beta_x - \tau - \pi_x - \tau$ -echo sequence. For the starting condition  $\rho_{0,S}$  the signal intensity is given as [4]

$$S_x(\tau) = -\sin[2(d - J)\tau] \cos^2\xi (\sin\beta 2\sin^2\xi + \sin 2\beta \cos^2\xi)/2 \quad [4]$$

while one obtains for  $\rho_{0,C}$  and  $\theta=0$

$$S_x(\tau) = \sin[2(d - J)\tau] \cos^2\xi [\sin\beta \sin 2\xi - \sin 2\beta (2 + \sin 2\xi)/2]$$

and for  $\theta=\pi$

$$S_x(\tau) = -\sin[2(d - J)\tau] \cos^2\xi [\sin\beta \sin 2\xi + \sin 2\beta (2 - \sin 2\xi)/2]$$

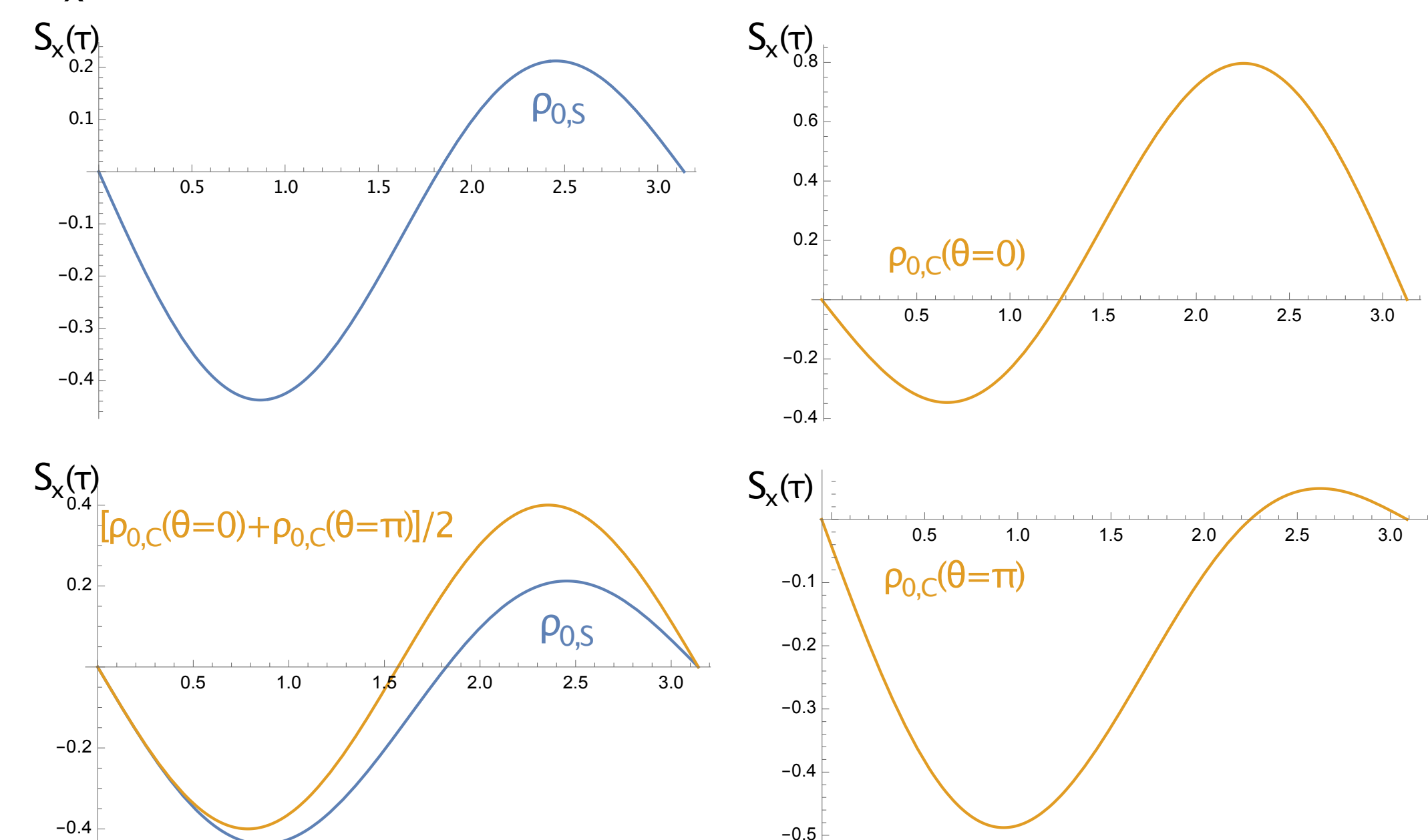


Figure 3. Comparison of the flip angle  $\beta$  dependence of the OOP-ESEEM signal  $S_x(\tau)$  for standard and CISS ET ( $\xi = \arctan(0.5)$ ).

## References

- [1] Naaman, R., Paltiel, Y., Waldeck, D. H. (2019) Nat. Rev. Chem. 3, 250-260
- [2] Carmeli, I. *et al.* (2014) Ang. Chem. Int. Ed. 53, 8953-8958
- [3] Chiesa, A. *et al.* (2021) J. Phys. Chem. Lett. 12, 6341-6347
- [4] Jeschke, G., Bittl, R. Chem. Phys. Lett. (1998) 294, 323-331

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