The study and manipulation of low dipole moment quantum states has been historically difficult due to their inaccessibility by conventional spectroscopic techniques. Controlling the spin in such states requires unfeasibly strong magnetic fields to overcome the typical decoherence rates. However, the advent of terahertz technology and its application to magnetic pulses opens up a new scenario. In this article, we employ an electron-hole pair model to demonstrate that it is possible to control the precession of the spins and to modify the transition rates to different spin states. Enhancing transitions from a bright state to a dark state with different spin means that the latter can be revealed by ordinary spectroscopy. We propose a modification of the standard two-dimensional spectroscopic scheme in which a three laser pulse sequence is encased in a circularly polarised magnetic pulse, whose role is to induce ultrafast coherent transitions between a bright and a dark spin state making the latter susceptible to spectroscopic investigation.

**INTRODUCTION**

Due to their slow decoherence rates dark states often play a fundamental role in a wide variety of fields touching the quantum realm. Ranging from quantum optics to solid state physics, dark states are essential for understanding phenomena of energy and charge transport at the quantum level. In quantum information, dark states create decoherence-free subspaces, supporting long-lived quantum coherence [1]. Dark charge transfer states support efficient charge transport and charge separation in natural and artificial light harvesting complexes [2–4]. Efficient transport within quantum wells and two-dimensional materials or optical control in solid-state and semiconductor systems are all critically dependent on different manifestations of dark states [5–7]. Moreover, several new physical effects such as electromagnetically induced transparency, subrecoil laser cooling or ultracold molecules owe their discovery to the role played by dark states [8–10].

As the degree of control on the dynamics of quantum systems increases, it becomes necessary to fully comprehend the influence exerted by all the degrees of freedom that interact with the system. Mastering dark states holds the potential to all-optical control of quantum systems, which, combined with the possibility of spintronics, opened up by the capability of addressing single spins with magnetic pulses. This line of research offers intriguing possibilities in quantum technological applications, such as quantum computing or sensing.

Detection of dark states remains challenging; one option is to utilise laser light with sufficiently high intensity to couple beyond the dipole order, thereby enabling forbidden transitions. However, such a method is typically not possible in most applications, systems and materials, as the employed light intensities have to be small enough to prevent bleaching or destruction of the sample. Another possibility is to employ indirect detection techniques such as the dark state’s low fluorescence yields [11,12], or more conventionally by employing modified or engineered samples that either displace or do not contain the supposed dark state (which allows its detection by comparison of spectra [3,13,14]). Time resolved Two-Dimensional Electronic Spectroscopy (2DES) has emerged as the most comprehensive technique for the study of dynamics, due to its versatility and by its main characteristic of resolving a non-linear signal in excitation and emission frequencies [15]. In this article, we will propose a modification of 2DES that allows one to directly detect and measure spin-dependent dark states.

Despite its success, 2DES alone still relies on the strength of transition dipole moments in the investigated samples and is therefore ill-suited for the study of dark states by their absorption or fluorescence properties. 2DES can go beyond the scope of linear methods, however, by detecting excited state absorption (ESA) signatures of dark states. Depending on the properties of the sample, this signature may be nonetheless shifted out of the detection range of the experiment [16], or be buried under stronger ESA-signals. Generally, ESA-features may be broad, featureless, convoluted, and therefore hard to analyse [17,18]. We argue that, apart from the linear spectroscopic signal and ESA-signatures, there are other properties of quantum states that can be exploited to make dark states responsive to spectroscopic probing.

It was recently demonstrated that a static magnetic field can manipulate charge transfer states, owing to the non-trivial spin and small Coulomb binding properties [2]. Moreover, these states can be inferred through the behaviour of the resultant photocurrent when affected by magnetic fields of varying intensity [19]. In particular, it was shown that a magnetic field can be used to induce coherent transitions from a bright singlet charge transfer state to a dark triplet charge transfer state. This result suggests that the same principle could be applied to any such dark state that is spin-connected to a bright state. However, for most applications and even for the highest magnetic fields, the time-scales in which static magnetic fields are able to modify the evolution of spin-states is nanoseconds at most, far from the 2DES femtosecond scale. The latter is nonetheless necessary to detect quantum states before decoherence dominates. The solution we propose in this article is employ-
due to the spectral resolution of the conventional 2DES scheme (see Fig. 1), we demonstrate that states bright. By combining such a magnetic pulses with a pulse (violet displays the fully non-collinear phase matching geometry of the laser pulses sequence) induces coherent transitions from the excited bright state to a dark state. The second pulse stabilises the population in the dark state while the third produces a rephasing signal. (b) displays the fully non-collinear phase matching geometry of the laser pulses which in our design are immersed in a magnetic pulse (violet filled curve).

![Figure 1.](image)

**Figure 1.** Schematic representation of the proposed magnetic field enhanced two-dimensional spectroscopic experiment. In (a) the three laser pulse sequence is shown. The first pulse excites a bright state in the system, which evolves freely for a variable time \( \tau \) (coherence time), during which the magnetic pulse (which acts all through the laser pulses sequence) induces coherent transitions from the excited bright state to a dark state. The second pulse stabilises the population in the dark state while the third produces a rephasing signal. (b) displays the fully non-collinear phase matching geometry of the laser pulses which in our design are immersed in a magnetic pulse (violet filled curve).

2DES WITH A MAGNETIC PULSE

The development of the theory of nonlinear spectroscopy [20], together with the progress of ultrafast laser technologies and multidimensional spectroscopic methods [21] represented a decisive step forward in the study of dynamics in condensed-matter quantum systems. The result was a deeper understanding of processes such as light absorption, energy transport, and quantum dynamics in open systems. 2DES represents a recent highlight in this development [15][22][30].

2DES is a powerful technique to study nuclear and electronic correlations between different transitions or initial and final states. It utilises three ultrashort, spectrally broad laser pulses separated by controlled time delays (see Fig. 1(a)). The Fourier transform of the system response with respect to the coherence time \( t_1 \) (time between the first and second pulses) and with respect to the rephasing time \( t_3 \) (time between the third pulse and the signal) yields a 2D spectrum in the frequency domain which correlates absorption and emission frequencies at each population time \( t_2 \) (time between the second and third pulses). To increase the number of coherent superpositions between quantum states, broad-band excitation lasers are used. Each specific feature in the 2D spectrum will then correspond with one superposition between quantum states and will provide real-time information about the both population and coherence dynamics in the system.

The theoretical simulation of the 2DES requires calculating the third-order, non-linear response function for the polarisation of the system in an electric field, which is expressed as

\[
P^{(3)}(r,t) = \int dt_3 \int dt_2 \int dt_1 S^{(3)}(t_3,t_2,t_1) E_3(r,t-t_3)E_2(r,t-t_2-t_3)E_1(r,t-t_3-t_2-t_1),
\]

where \( E_j \) are the pulse electric fields at different time delays. \( S^{(3)}(t_3,t_2,t_1) \) describes the third order non-linear response of the material and relates the driving fields at \( t_1, t_2 \) and \( t_3 \) to the induced nonlinear polarization at time \( t \). The response function contains information about the relevant quantum states of the sample, all possible optical transitions between them at time \( t_1, t_2 \) and \( t_3 \) and their evolution when they are not interacting with the fields. \( S^{(3)}(t_3,t_2,t_1) \) is only defined for positive times and reads

\[
S^{(3)}(t_3,t_2,t_1) = \left\langle -\frac{i}{\hbar} \mu(t_3 + t_2 + t_1) [\mu(t_2 + t_1), \mu(t_1), \mu(0), \rho(-\infty)] \right\rangle > 0,
\]

where \( \mu(t) \) represents the dipole-dipole interaction at time \( t \). The simulations are then performed writing the operator in the Heisenberg representation by replacing \( \mu(t) \) by \( \exp(iH(t_1)\mu(0)\exp(-H(t_1)) \). For time-independent Hamiltonians, the computational effort is greatly reduced by computing the time evolution due to the final laser pulse and correlating it with all the possible time orderings of the initial pulses; calculation of all possible time orderings one by one can therefore be avoided.

In this article, we introduce a magnetic pulse that is acting on the sample through the duration of the laser pulses sequence (see Fig. 1); consequently, the Hamiltonian now depends explicitly on time. To optimise the time needed to perform the numerical simulations including the magnetic pulse, we are going to calculate Eq. (2) using a methodology that requires acting with the dipole-dipole operator in both the left “bra” and right “ket” of the density matrix of the system. In order to reduce the simulation time, the magnetic field will no longer be a unique pulse that oscillates during the whole duration of the laser pulse sequence; instead, the magnetic pulse is going to change its phase, at discrete time intervals, every time a laser pulse is applied in the simulation. This means the oscillating component of the laser pulse will have a non-physical random phase added in the simulations. These non-physical phases will not affect the accuracy of the simulation procedure; this approximation is justified because the relevant operation to recover the properties of the system is the action of the magnetic field throughout the population time.
MODEL

To illustrate the mechanism of the magnetic field enhanced 2DES, we use a minimal model containing a spin one single electron-hole (e-h) pair whose dipole moment is low but not zero, and its counterpart triplet state, which is completely dark. We choose the e-h pair to have low Coulomb binding, representing states which are known as charge transfer, polaron, or simply exciton states. Our choice is based on the importance that these states have in a wide variety of systems ranging from quasi 2D quantum wells to natural and artificial light conducting and harvesting systems \cite{5, 6, 31-34}. Low Coulomb binding bright states are expected to have low dipole moments. Moreover, owing to the loose nature of the e-h Coulomb binding in charge transfer states, they will be less sensitive to strong magnetic fields. States with just one electron are easier to manipulate with a magnetic field; composite states with stronger binding will typically have a higher dipole moment and will provide a clearer optical signal.

The absence in our model of a singlet exciton state, which is usually present together with charge transfer states, imposes yet more restrictive limits to the dipole moment of the singlet charge transfer state. The formation of tightly bound exciton states occurs faster than the formation of charge transfer state. The formation of tightly bound exciton electron-hole (e-h) pair whose dipole moment is low but not zero, and its counterpart triplet state, which is completely dark with respect to the electronic ground state as spin transitions are prohibited upon excitation. An appropriately tuned external magnetic pulse, $B(t)$, is able to induce spin flips on the individual components of an e-h pair by modifying the precession frequency of the spins. Consequently, a magnetic pulse is used to transfer population from the singlet state to the spin zero triplet state. Subsequently, according to Eqs. \ref{3} the magnetic pulse may transfer population to and among the spin $\pm$ one states.

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Each of the operators in Eq. \ref{3} describes a different incoherent process happening at a particular rate $\gamma$ that characterises the environment. In our model, we will consider these as rates empirically defined numbers. Notice that in the proposed experimental scheme, rates in the femtosecond can be inferred from the experimental data. Thus, no \textit{a priori} knowledge is necessary.

TERAHERTZ INTER-SYSTEM CROSSING

Nowadays, controlling spins with an external magnetic field is technically achievable \cite{35, 37}. Terahertz magnetic field pulses have become only recently available \cite{38, 39}, offering the possibility of accessing ultrafast magnetisation dynamics on the femtosecond time-scale \cite{40, 46}. Moreover, (and contrary to what happens with laser spin manipulation methods) magnetic pulses overcome the problem of undesired electronic excitations and potentially destructive thermal effects \cite{47}. They thus represent a non-invasive technique to address individual spins.

To produce spin flips— as it is needed for inter-system crossing— the coupling induced by the magnetic field has to be strong enough to ensure that the precession of the spins is faster than the relaxation time of the states. However, the typical coupling of an electron (hole) to a magnetic field is mediated by the Bohr magneton and the Landé factor. The small value of these two factors in typical e-h pairs has to be compensated with a magnetic field of at least kiloteslas in order to produce the sub-picosecond inter-system crossing necessary for having an effect on the 2D spectra \cite{22}. Such magnetic fields are beyond any experimental instrument available.

\begin{equation}
\mathcal{L} = \sum_{\alpha} \gamma_{\alpha} \left[ \sigma^\alpha \rho(t) \sigma^\alpha_{\alpha} - \frac{1}{2} \left\{ \sigma^\alpha \sigma^\alpha_{\alpha}, \rho(t) \right\} \right]. 
\end{equation}
nowadays, and would be likely to disrupt the sample. To circumvent the limitation, we propose employing terahertz magnetic pulses, whose interaction with the spin components is strong enough to produce the necessary spin flips \[48\]–\[51\]. As we demonstrate in this article, the key factor which allows to reduce the magnitude of the fields employed, is not the interaction strength, but rather the frequency with which the magnetic pulse oscillates. Note that we will still be working in the strong coupling regime, as the amplitude of the fields must still be big enough for a sufficient coupling. As such, typical fields are around one Tesla.

The interaction of a spin in an external oscillating magnetic field is governed by the equation \( S = B \times S \), which provides the Hamiltonian that describes the dynamics of a spin pair \[52\]. Choosing the magnetic field to have components both in the \( z \) and \( x \) directions \( (B = B_z + B_x) \), the Hamiltonian for a charge transfer motion reads

\[
H = B_z S_z^2 + B_x S_x^2 + 2B_y(S_z^2 + S_y^2),
\]

where each component \( B_{e,h} \) references the total magnetic field acting on either the electron or the hole. \( B_{e,h} \) includes any source of magnetic interaction, i.e. the external magnetic pulse and the hyperfine component felt by the spin. However, for the purposes of this article, the external magnetic field is always going to be much stronger than any local hyperfine magnetic field; hence, the hyperfine contribution can be safely disregarded from the calculations and we will not consider it further. \( B_{e,h}(B_z) \) in Eq. \( 4 \) already includes the coupling of the magnetic field with the spin in the form \( g_{\mu_B}/2 \), with \( g \) being the Landé factor and \( \mu_B \) the Bohr magneton constant. The Landé factor is specific for either the electron or the hole.

The equations of motion are better understood in the singlet-triplet basis spanned by the total spin of the charge transfer state. The dynamics will describe the motion in terms of four functions for \( S(t), T_-(t), T_0(t) \) and \( T_+(t) \), which represent the four possible spin one states of an e-h pair. This base is a logical choice as excitation by an incoming photon occurs directly in such states (we assume the impulsive limit in which the laser pulses is much faster than any other timescale in the dynamics). The time evolution for such states is calculated employing the Heisenberg equation with the Hamiltonian Eq. \( 4 \), transformed to the exciton basis

\[
\frac{dS}{dt} = -i\Gamma S - i\delta_0 T_0, \\
\frac{dT_0}{dt} = -i\delta_0 S - i\sqrt{2}B(T_++T_-), \\
\frac{dT_+}{dt} = -i\tilde{B}T_+ - i\sqrt{2}B T_0, \\
\frac{dT_-}{dt} = i\tilde{B}T_- - i\sqrt{2}B T_0.
\]

In principle, the equation of motion for the singlet state \( S(t) \) in Eq. \( 5 \) includes a relaxation term \( \gamma S(t) \) that describes geminate recombination or dissociation of the spin pair. In practice however, relaxation of the singlet charge transfer states occurs on time-scales much longer than those probed on a 2DES experiment, where processes of decoherence and dephasing are dominant. Therefore, we will consider \( \Gamma = 0 \) henceforth. Triplet states do not include relaxation terms, as they relax on a much longer time-scale. This is generally true for any dark state and thus valid in our experimental scheme for any spin state model.

In Eqs. \( 5 \), \( B \) represents the magnetic field, while \( \delta_0 \) and \( \tilde{B} \) are, respectively, the difference and sum of the interaction of the magnetic field with each of the spins, i.e. \( \delta_0, \tilde{B} = \frac{\hbar}{2}g_{\mu_B}/2 \). From these equations two conclusions emerge immediately: first, why it is required that the Landé factor has to be different for the electron and the hole, for otherwise the dynamics would be trivial. And second: the magnetic field must exhibit \( z \)- and \( x \)-polarisation components. The previous point relates to the aim of spin state mixing not only between the singlet and triplet spin zero states –both polarised along the \( z \)-direction– but also among the three triplet spin states, which will be Zeeman split and therefore, will show up as distinct peaks in a 2D map.
The magnetic pulse is described by the equation

$$B = B_0 \sin(\omega t) \exp \left[ \frac{(t - t_0)^2}{2\sigma_t^2} \right], \quad (6)$$

with an oscillating component and a Gaussian envelope. In Figs. 3(a) and (d), we represent two possible examples of magnetic pulses. In both cases, the amplitude of the pulse $B_0$ is chosen to be 1 Tesla while the frequency is correspondingly in the terahertz domain with $\omega$ in Fig. 3(a) an order of magnitude bigger than in Fig. 3(c). In both upper and lower panels on Fig. 3(a) the initial state witnesses the spin singlet charge transfer state (Figs. 3(b) and (e)) completely populated while the three triplet states have no population at all. Initially, as the pulse interacts with the spin pair, the population is partially transferred to the spin zero triplet charge transfer state and afterwards into the spin $\pm 1$ triplet charge transfer states, as represented in Figs. 3(c) and (f) (only the spin $+1$ case is shown as the spin $-1$ behaves in exactly the same way).

The response of the spin states to the pulse depends on whether or not a resonance condition is fulfilled. A resonant pulse produces coherent Rabi oscillations that vanish as the pulse ends. In this case, very clean oscillations in the population of the charge transfer states can be observed, but there will be no final steady state population in the dark triplet charge transfer state. On the other hand, working out of resonance means a) that several frequency components show up in the population oscillations and b) that the steady state after the pulse has ended shows population in all four spin charge transfer states, which will decay on a slow timescale. Consequently, effective population transfer to the triplet states occurs with pulses as the one represented in Fig. 3(c). We conclude that for the purposes of this article where clean oscillations are ideal, resonant pulses are much better suited, while for applications where the interest lays in transferring populations and controlling the spin states, off-resonant pulses would be required.

**DARK STATES DETECTION**

We simulate the dynamics of a singlet-triplet system interacting with a resonant magnetic pulse in different spectroscopic configurations. The magnetic pulse is chosen to have amplitude $B_0 = 1$ T, oscillation frequency $\omega = 1$ THz, and a Gaussian envelope that guarantees the pulse has approximately constant amplitude through the duration of the laser sequence simulation, namely $> 400$ fs. Initially, dipole moment is associated only with the singlet state, meaning that the triplet state is completely dark in all the simulations. Consequently, in the absence of a magnetic field, the only contribution comes from the singlet charge transfer state absorption. We note that the model presented here is not substantially altered by marginal singlet-triplet coupling or non-zero dipole moment of the dark state.

2DES is a costly technique and its use has to be well-motivated when simpler spectroscopy techniques might suffice. In Fig. 3(a), we plot the absorption spectrum in the absence and in the presence of a magnetic pulse. These results demonstrate that, while in absence of B-induced interaction, there is only one absorption peak corresponding with the singlet state. In the presence of such an interaction, a complicated spectral signature emerges. However, any further analysis is hampered by the convoluted character of the signal, leading to complicated lineshapes.

Moving on to time-resolved methods, transient absorption spectroscopy (pump-probe) yields information about the energy of the quantum states and the transition and relaxation rates among them. In Fig. 4(b), we plot the pump-probe spectrum. In the absence of a magnetic field, the lineshape of the singlet absorption peak is a well-defined Lorentzian. Similar to the case of the linear spectrum discussed above, the spectral features are convoluted in a non-trivial manner in the presence of a magnetic field. Thus, even in a model with only four states, interpretation becomes difficult, as the spectral features in the presence of a magnetic field cannot be decomposed in a simple sum of Lorentzians. Since the only source of peak splitting is the magnetic pulse, resolution depends on the interaction strength of the magnetic pulse with
the electron and the hole, which is in principle unknown. The information about the interaction is encoded in the coherent transport among states, conspicuous either as oscillations in the population peaks or as distinctive features in 2DES. Inasmuch as transient absorption spectroscopy generates intricate spectra, 2DES with its fully resolved spectra, is the natural choice to study dark states through a magnetic pulse.

In Fig. 5, we plot the real part of the spectrum resulting from the sum of all rephasing and non-rephasing components. The polarization of the excitation pulses was set to all-parallel. Such a configuration yields the strongest overall 2D-signal, but will also contain coherence dynamics from intramolecular vibrational states [53], which is readily accounted for in simulations. Fig. 5(a) displays a characteristic absorption peak corresponding with the singlet state which in absence of a magnetic pulse is the only bright state of the system. Interaction of the states with a magnetic pulse through the duration of the 2DES sequence produces a spectrum richly populated with distinctive features in Fig. 5(b).

Focusing the analysis on the central part of the spectrum, we observe several peaks along the diagonal (see also Figs. 4(a) and(b)) that correspond to absorption peaks from different states composing the system. We are witnessing the triplet dark states mixed with the singlet state by the magnetic pulse. In addition, the numerous crosspeaks correspond to the different coherences that gather the information of population transfer from singlet to triplet states and among triplet states, according to Eqs. 5.

We have demonstrated that 2DES can reveal the presence of dark states if supplemented with a magnetic pulse. As a next step, we reconstruct the properties that characterise these dark states. In Eq. 7, we present the original Hamiltonian which needs to be reconstructed. The diagonal terms are the energies of the states prior to the interaction with the magnetic pulse with an extra term we name $Z$ accounting for the Zeeman splitting. The non-diagonal terms are the different interactions according to Eqs. 5. Conversely, the diagonal peaks in the 2D spectrum in Fig. 5(b) provide information about the exciton energies, namely, about the eigenvalues of Eq. 7. Therefore, to reconstruct the original energies we need the interaction terms of Eq. 7 and then revert the diagonalisation procedure.

$$\mathcal{H} = \begin{pmatrix}
S & 0 & A & 0 \\
0 & T^{-1} - Z & B & C \\
A & B & T^0 & B \\
0 & C & B & T^{+1} + Z
\end{pmatrix}.$$  \hspace{1cm} (7)

The diagonal peaks in Fig. 5(b) are located at 1.342, 1.375, 1.396, and 1.428 eV. The information about the interaction terms is encoded in the non-diagonal peaks of Fig. 5(b). The location of these peaks tells us about between which two states the coherence transport is happening. The frequency of oscillation of these peaks in population time encodes the information about the interaction strength between energy levels. Hence, after a multi-exponential fitting to get rid of dephasing, the Fourier transform in population time of the non-diagonal peaks provides us with the interaction terms. These give us the following numbers: 0.008 eV for $A$, 0.04 for $B$, and 0.009 for $C$. With them we obtain that the interaction of the magnetic pulse with the electron and the hole is 110 meV, which gives us a Zeeman splitting of 1.4 meV and a reconstructed states at 1.415, 1.392, 1.389, and 1.387 eV. Hence we are able to reconstruct the original states with an error smaller than 2%.

Figure 5. Numerical simulation of 2DES in the model with a singlet and triplet charge transfer states with energies in 1.4 and 1.39 eV respectively. In (a), in the absence of a magnetic pulse the absorption peak corresponding to the singlet charge transfer state. In (b), the action of a magnetic pulse of frequency 1 THz and amplitude 1 Tesla, with an envelope that guarantees the pulse duration for the whole experiment, permits population transfer from the singlet to the various triplet charge transfer states, as evidenced by several diagonal peaks and non-diagonal structures which demonstrate the presence of coherent transport among different quantum states. The latter are Zeeman split, with a gap of 1 meV. The coupling strength of the magnetic pulse to the charge transfer states is 100 meV while the lifetimes are 80 fs for the singlet charge transfer state and 200 fs for the triplet components. Both plots are at population time 90 fs.
CONCLUSIONS

Summarising, we propose and test numerically a modified version of 2DES in which a terahertz magnetic pulse is employed to create coherent population transfer from a bright spin singlet electron-hole pair to the components of the corresponding triplet state. The magnetic pulse is able to modify the spins precession in a time-scale relevant for 2DES. The effect can be understood as a dipole moment redistribution that allows transitions from the ground state to the triplet states, which then appear as distinctive peaks in the 2D-spectrum. State reconstruction from the position of the peaks and the oscillation frequencies of the coherences allows one to infer the properties of the original states, a feature that simpler spectroscopic techniques do not allow either for lack of information or lack of resolution.

The magnetic pulse employed to demonstrate the feasibility of the proposal is realistic by today standards. The parameters describing the charge transfer states are as well within the typical range. Tuning the magnetic pulse so as to produce the maximum effect requires some work, as it is the balance between the amplitude of the pulse and the frequency that dictates the transfer rate among states and the frequency at which the coherences will oscillate. Nonetheless, the split of peaks and the unveiling of dark states is observed for almost any sensible magnetic pulse; it is therefore easy to obtain a first estimation that permits fine-tuning the experiment. The strength with which the magnetic pulse couples to the spin states depends on the nature of the later, and has to be elucidated experimentally. However, knowing the value of this coupling is necessary in order to reconstruct the in principle unknown energies of the states analysed. Hence the need for 2DES experiments is warranted.

Notice that different kinds of dark states with different spin configurations will have different equations of motion than Eq. (5), and the constraints imposed by the Landé factor will not necessarily apply. However, the background physics remains unchanged, and any spin dark state can be manipulated so. Therefore, the conclusions obtained in this article are valid for a wide class of dark states.

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[1] D. A. Lidar, I. L. Chuang, and K. B. Whaley, *Phys. Rev. Lett.* **81**, 2594 (1998)
[2] S. Oviedo-Casado, A. Urbina, and J. Prior, *Scientific Reports* **7**, 4297 (2017)
[3] M. Ferretti, R. Hendrikx, E. Romero, J. Southall, R. J. Cogdell, V. I. Novoderezhkin, G. D. Scholes, and R. Van Grondelle, *Sci. Rep.* **6**, 1 (2016)
[4] Z. Hu, G. S. Engel, F. H. Alharbi, and S. Kais, *The Journal of Chemical Physics* **148**, 064304 (2018)
[5] D. Snoke, S. Deney, Y. Liu, L. Pfeiffer, and K. West, *Nature* **418**, 754 EP (2002)
[6] Z. Ye, T. Cao, K. O’Brien, H. Zhu, X. Yin, Y. Wang, S. G. Louie, and X. Zhang, *Nature* **513**, 214 EP (2014)
[7] C. G. Yale, B. B. Buckley, D. J. Christle, G. Burkard, F. J. Herrmann, L. C. Bassett, and D. D. Awschalom, *Proceedings of the National Academy of Sciences* **110**, 7595 (2013)
[8] K.-J. Boller, A. Imamoglu, and S. E. Harris, *Phys. Rev. Lett.* **66**, 2593 (1991)
[9] A. Aspect, E. Arimondo, R. Kaiser, N. Vansteenkiste, and C. Cohen-Tannoudji, *Phys. Rev. Lett.* **62**, 826 (1988)
[10] G. Morigi, J. Eschner, and C. H. Keitel, *Phys. Rev. Lett.* **85**, 4458 (2000)
[11] D. Egorova, *The Journal of Chemical Physics* **142**, 212452 (2015)
[12] E. L. Read, G. S. Schlau-Cohen, G. S. Engel, T. Georgiou, M. Z. Papiz, and G. R. Fleming, in *Ultrafast Phenomena XVI*, edited by P. Corkum, S. Silvestri, K. A. Nelson, E. Riedle, and R. W. Schoenlein (Springer Berlin Heidelberg, Berlin, Heidelberg, 2009) pp. 559–561.
[13] M. Krecik, S. M. Hein, M. Schoth, and M. Richter (2015) pp. 9361 – 9361 – 10.
[14] D. J. Berkeland and M. G. Boshier, *Phys. Rev. A* **65**, 033413 (2002)
[15] D. M. Jonas, *Annual Review of Physical Chemistry* **54**, 425 (2003)
[16] O. Bixner, V. Lukeš, T. Mančal, J. Hauer, F. Milota, M. Fischer, I. Pugliesi, M. Bradler, W. Schmid, E. Riedle, H. F. Kauffman, and N. Christensson, *The Journal of Chemical Physics* **136**, 204503 (2012)
[17] T. Polívka and V. Sundström, *Chemical Reviews* **104**, 2021 (2004)
[18] V. Perlík, J. Seibt, L. J. Cranston, R. J. Cogdell, C. N. Lincoln, J. Savolainen, F. Šanda, T. Mančal, and J. Hauer, *The Journal of Chemical Physics* **142**, 212434 (2015)
[19] S. Oviedo-Casado, A. Urbina, and J. Prior, *Eur. Phys. J. Special Topics* **227** (2018).
[20] S. S. Mukamel, *Principles of nonlinear optical spectroscopy* (New York : Oxford : Oxford University Press, 1995) includes index.
[21] P. Hamm, M. Lim, and R. M. Hochstrasser, *The Journal of Physical Chemistry B* **102**, 6123 (1998)
