# The time-scale of nonlinear events driven by strong fields: Can one control the spin-coupling before ionization runs over?

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**Abstract.** An initially populated spin manifold interacting with an external field can decay via spin-coupling or via ionization. Using a simple two-level Hamiltonian we investigate the relation between spin coupling and ionization rate and identify conditions for an efficient spin-control by suppressing ionization. The results are confirmed in solving the time-dependent Schrödinger equation for the interaction of a laser field with a spin-coupled model system where two electrons and a nucleus move in a collinear configuration. It is thus shown, that quantum control of intersystem crossing can indeed be effective if the intensity of the external field and the accompanying Stark-shift is adjusted properly to the spin coupling-strength.

## 1. Introduction

With the development of ultrafast and ultrastrong laser pulses, many nonlinear processes in molecules have been observed and controlled experimentally [1, 2]. Aside from enabling multi-photon excitation pathways, a strong field induces large Stark shifts that can deeply alter the structure of the electronic potentials [3, 4, 5, 6, 7]. These effects have been used to induce molecular alignment [8, 9, 10, 11, 12, 13, 14], to assist selective population transfer between vibronic states [15, 16, 17, 18, 19, 20], to control photodissociation reactions [21, 22, 23, 24, 25], modify the rate of photochemical processes [26, 27, 28, 29] or even change the bond length of molecules [30, 31, 32, 33, 34].

We are interested in the control of spin transitions via a particular optical control strategy, based on the nonresonant dynamic Stark Effect (NRDSE) [21, 22]. By Stark shifting the electronic spectra in the presence of a strong nonresonant field, one can force the decoupling of the singlet and triplet states on a system with otherwise fast intersystem crossing. However, the presence of strong fields triggers many other (unwanted) nonlinear processes, in particular multi-photon absorption to excited singlet (and triplet) states and, more importantly, multi-photon ionization. In this work we characterize the conditions required to control the spin transition on a time-scale shorter than the onset of ionization. In particular we show under what intensities one observes a change from Stark-shift driven (i.e. controlled) to ionization driven driven dynamics, setting limits for the maximum values of the spin couplings under which the system is controllable via an NRDSE process.

The accurate calculation of the rate of ionization under strong fields, beyond perturbation theory, is a difficult enterprise that, nonetheless, has become quite important with the birth of attosecond Physics [2]. For two-electron systems, grid-based propagation schemes using regularized soft-core Coulomb potentials [35, 36, 37] in few dimensions (for instance, one dimension per electron) provide a reasonable ground for the evaluation of dynamical processes where both multi-photon and tunneling ionization can occur. In previous work we have studied the interplay between nonlinear field processes, coupled electron and nuclear motion and singlet-triplet transitions. We have developed the extended Shin-Metiu model (ESM) [47] based on the original Hamiltonian introduced by Shin and Metiu to study charge transfer processes in solids with screened Coulomb potentials [38, 39, 40, 41, 42, 43, 44, 45]. The ESM model is a dynamical model incorporating three degrees of freedom (3D) for a proton and two collinear electrons moving between two fixed ions, allowing transitions between the singlet and triplet components of the electronic wave function. Although much flexibility exists in the choice of parameters, for symmetrical couplings between all particles (equal charges and screenings) the ESM favors symmetrical arrangements where the moving ion is placed in between both fixed ions and each electron is in between one fixed ion and the central ion. When the separation between the fixed ions is large, e.g. $R = R_2 - R_1 \geq 10$Å, two nuclear equilibrium geometries exist. In this regard, a molecular analogue of the present ESM structure conceivably looks more like an isomeric system rather than a diatomic molecule.

In this work we do not incorporate effects associated with the rotational degree of freedoms. An off-resonant field creates an angle-dependent potential so that, in general, the

angular motion should be included in a theoretical description [46]. In neglecting rotations we adopt the reasonable approximation that the latter are too slow in comparison with the relevant time-scales (of ST-transitions and ionization, respectively) which here are in the femtosecond regime for the large coupling case. It is thus reasonable to treat the nuclear frame as frozen with respect to the rotational motion. Otherwise one can consider the ESM model as a prototype for systems with limited rotation.

In addition, because of the large separation between the two electrons in average, the energies of the here relevant singlet and triplet states are almost degenerate, specially around the equilibrium geometries. Since the electronic wave functions come on pairs of symmetric (singlet) and antisymmetric (triplet) states under exchange of electron coordinates, $z_1$ and $z_2$, any extra term in the Hamiltonian that is an odd function of $z_1 - z_2$ acts as a very effective source of spin-coupling between the near degenerate states. The spin coupling is then essentially that of a two-level problem.

In our former work [47, 48] we tuned the parameters of the ESM Hamiltonian to force spin switching from the ground electronic singlet state to a degenerate electronic triplet state in 120 fs. We then showed that it is possible to control the spin transition, locking the spin populations, while at the same time minimizing multi-photon absorption [48]. However, by solving the time-dependent Schrödinger equation (TDSE) on a 3D grid we also found that the rate of ionization is much faster than the natural (laser-free) duration of the spin transition, making the whole NRDSE scheme finally ineffective [47]. In this work we analyze the conditions that are required to turn around this conclusion. The solution of the TDSE with the ESM Hamiltonian involves cumbersome numerical calculations that do not permit an easy evaluation of the interplay of different Hamiltonian parameters, particularly when they lead to opposite effects that are important in controlling the dynamics. In Section 2 we build a minimal Hamiltonian for a two-level system with polarizable spin states (Stark effect), intramolecular spin couplings and effective ionization. From this so-called 2-PSI Hamiltonian we obtain analytical expressions for the time-scales of ionization and spin-transfer, using a simple model for the ionization as a function of the field amplitude. We show under what conditions, that is, for what spin-coupling strengths, it is possible to decouple the spin transition before the onset of ionization. In Section 3 we use the numerical calculations from the ESM dynamics to fit the parameters of the 2-PSI model in order to obtain reasonable estimates of the ionization rates within the framework of the simple model. The analytical expressions are then used as a guide to find the laser intensities for a given spin coupling that allow to decouple the spin states before substantial ionization occurs. The actual test whether control is possible is then carried out in Section 4 using the fully numerical ESM model for different coupling strengths. Finally, Section 5 contains the conclusions.

## 2. The 2-PSI Model

In order to understand the control of the spin transfer via nonresonant Stark effect and the role of the ionization, we first propose a simple two-level Hamiltonian which includes the effect of Stark shifts on a singlet and a triplet state coupled to each other via a spin interaction term

$V_{ST}$. This model is the same as used in [48] but we include here an effective ionization rate $\Gamma$ that we regard, for simplification, equal for the singlet and triplet states

$$\mathsf{H}_{\text{eff}} = \begin{pmatrix} -i\Gamma(\varepsilon) & V_{ST} \\ V_{ST} & \Delta(\varepsilon) - i\Gamma(\varepsilon) \end{pmatrix} \tag{1}$$

where the Stark-shift is

$$\Delta(\varepsilon) = \Delta(0) - (\alpha_T - \alpha_S)\varepsilon^2/2 \tag{2}$$

and we will make $\Delta(0) = 0$ as in the ESM, where the ground singlet and triplet states are degenerate. Atomic units will be used throughout unless otherwise stated. To simplify the notation we write $\alpha = |\alpha_T - \alpha_S|$.

The characteristic time for the spin transfer in the absence of the field is defined by

$$\tau_{ST} = \frac{\pi}{2V_{ST}} \tag{3}$$

In the presence of an external field, assuming for simplicity a constant envelope $\varepsilon$, integrating the time-dependent Schrödinger equation for the above Hamiltonian [Eq.(1)] gives for the triplet population:

$$P_T(t) = e^{-\Gamma t}\left(\frac{V_{ST}}{\Omega_e}\right)^2 \sin^2 \Omega_e t \tag{4}$$

with $\Omega_e = \sqrt{V_{ST}^2 + \Delta(\varepsilon)^2}$, and we assumed that initially, only the singlet state is populated, i.e. $P_s(t=0)$=1. The latter can be depopulated via ionization and spin transfer. The NRDSE gives a prescription to avoid the spin transfer: Use a field strong enough that $\Delta(\varepsilon) \gg V_{ST}$.

For instance, defining a maximum threshold value for the triplet population, $P_T^m$, provides, via Eq.(4), the minimum (threshold) for the Stark shift, $\Delta_m$. Let us first neglect ionization. From

$$P_T^m = \frac{V_{ST}^2}{V_{ST}^2 + \Delta_m^2} \tag{5}$$

we obtain

$$\Delta_m = V_{ST}\sqrt{\frac{1 - P_T^m}{P_T^m}} = V_{ST}\chi^{1/2} \tag{6}$$

where

$$\chi = P_S^m / P_T^m \tag{7}$$

is the relative singlet to triplet conversion at the threshold, when the singlet population is the minimum allowed. Clearly the control is possible as long as the polarizabilities of the singlet and triplet states are different enough, $\alpha > 0$. Since the Stark-shift is a quadratic effect in the field, the threshold value for the field intensity is, from Eq.(2)

$$\varepsilon_m^2 = \frac{2V_{ST}\chi^{1/2}}{\alpha} \tag{8}$$

Additionally, the field changes the time-scale of the spin transfer. If we define $\tau_e$ as the first time the triplet population is maximal, for large $\chi$ ($\Delta_m \gg V_{ST}$) one obtains

$$\tau_e = \frac{\pi}{2}\Omega_e^{-1} \approx \frac{\pi}{2}\frac{1}{\Delta_m} = \chi^{-1/2}\tau_{ST} \tag{9}$$

Now we go back to the ionization problem. The goal of the control is to avoid losing population from the singlet state neither from a spin transition nor from ionization. Given the above Hamiltonian [Eq.(1)] the task is difficult, as a strong field is needed to avoid spin transfer while the strong field immediately induces ionization via $\Gamma(\varepsilon)$. The key here is to find under which conditions the time-scale of the ionization is much slower than the time-scale of the spin-transfer, such that one can maintain the population in the initial state in the presence of the field for a time longer than $\tau_{ST}$.

We use here a simple but very general equation for the ionization as a function of the field

$$\Gamma = C\varepsilon_m^n \tag{10}$$

In a strong approximation the parameter $n$ can be related to the field frequency (twice the number of photons required to reach ionization). We simply regard Eq.(10) as an empirical model. Under this view the model is in fact quite general and roughly reproduces the ionization rate in the ESM Hamiltonian at short times, as we will show in the next section. Thus, the parameters of Eq.(10) for the PSI-model will be obtained by fitting the results of the numerical simulations using the ESM Hamiltonian. The model allows a simple relation between the time-scale of ionization and the field amplitude. Defining the characteristic time of ionization as the lifetime $\tau_{ion} = \ln 2\,\Gamma^{-1}$, and inserting the threshold field given by Eq.(8) for a fixed $\chi$ we obtain

$$\tau_{ion} = \frac{\ln 2}{C}\left(\frac{\alpha}{2V_{ST}\chi^{1/2}}\right)^{n/2} \tag{11}$$

The relation between the characteristic times of the spin-transfer and ionization is

$$\frac{\tau_{ST}}{\tau_{ion}} = \frac{\pi C}{2\ln 2}\left(\frac{2}{\alpha}\right)^{n/2}\chi^{n/4}V_{ST}^{(n-2)/2} = K\chi^{n/4}V_{ST}^{(n-2)/2} \tag{12}$$

where $K$ depends only on the non-spin-coupled part of the Hamiltonian that gives the spectra of the singlets and triplets and the ionization potentials (fixed for a certain set of parameters in the ESM model, for instance) and is thus approximately independent of $V_{ST}$. Although one can change the value of $K$ by playing with different pulse frequencies (thus changing the dynamic polarizability difference $\alpha$) for the ESM model we have found that it is clearly larger than 1 ($K \sim 40$) [49]

The same result with an extra $\chi^{-1/2}$ factor is obtained by comparing $\tau_{ion}$ with the time-scale for the spin transfer in the presence of the field

$$\frac{\tau_e}{\tau_{ion}} = K\chi^{(n-2)/4}V_{ST}^{(n-2)/2} \tag{13}$$

Clearly if $n = 2$, then $\tau_{ST}/\tau_{ion} = K\chi^{1/2}$, and the time-scales for ionization and spin transfer will be fixed by the non-spin-coupled part of the Hamiltonian. With $K \gg 1$ this makes

ionization the dominant process. However, for values of $n$ different than 2, it will be possible to privilege one process versus the other. We will show in the next section that for the ESM with symmetric parameters, $n > 2$. Thus the spin-transfer can be controlled before the onset of ionization in the regime of weak spin couplings or small $V_{ST}$.

## 3. Fitting the 2-PSI parameters with the ESM model: the ionization rate

Following the simple 2-PSI model, the most relevant parameter to determine if one can control the spin-transfer by a quadratic field effect (the Stark shift) before the ionization takes place, is the exponent $n$ that measures the dependence of the ionization rate on the field, which will depend on the Hamiltonian model.

We now turn to the full ESM Hamiltonian. The ESM couples the singlet manifold (symmetric wave functions) with the triplet manifold (antisymmetric wave functions). In matrix form:

$$\mathbf{H}_{\mathrm{ESM}} = \begin{pmatrix} H(z_1,z_2,Z) & \lambda(z_1-z_2) \\ \lambda(z_1-z_2) & H(z_1,z_2,Z) \end{pmatrix} \tag{14}$$

The coupling is chosen as the simplest antisymmetric form with the spin coupling strength given by $\lambda$. The diagonal part is the 3D Hamiltonian for the collinear motion of two electrons ($z_1$ and $z_2$) and one proton ($Z$) with mass $m$

$$H(z_1,z_2,Z) = -\frac{1}{2}\frac{\partial^2}{\partial z_1^2} - \frac{1}{2}\frac{\partial^2}{\partial z_2^2} - \frac{1}{2m}\frac{\partial^2}{\partial Z^2} + V(z_1,z_2,Z) \tag{15}$$

under an effective (screened) Coulomb type potential $V(z_1,z_2,Z)$. In what follows, In this work we vary $\lambda$. As a reference value, we use the coupling strength $\lambda_0 = 1.028 \cdot 10^{-3}$ eV/Å that was recently tested to control the spin-transfer dynamics [47, 48]. For this choice of parameters we observed $\tau_{ST,0} = 120$ fs. Here and in the following, a subindex "0" refers to results obtained with this set of parameters.

In order to fit the parameters of the 2-PSI model we solve the time-dependent Schrödinger equation on a 3$D$ grid with the ESM Hamiltonian [47, 48] using the split operator with fast Fourier transform [50, 51]. The spatial grid for the nuclear coordinate ranges from -4 Å to +4 Å, whereas the spatial grid for the electron coordinates is divided into an inner region ($|x|$ and $|y| \leq 10$ Å) and an outer region ($|x|$ or $|y| > 10$ Å) where the wavefunction is damped by an absorbing boundary. Assuming that ionization is effective in the outer region, the non-ionized population corresponds to the norm of the wavefunction in the inner region.

Since we are interested only in the rate of ionization as a function of the field, the spin coupling is set to zero ($\lambda = 0$) in these simulations in order to avoid spin transfer. The envelope of the electric field is a $\sin^2$-function which rises from time $t$ = 0 to 50 a.u. (1.21 fs) to its maximum and is then kept constant at the latter value. The remaining, non-ionized population $P_{ni}(t)$, which corresponds to $P_S(t)$ in the 2-PSI model, was calculated for different values of the field amplitude $\varepsilon$ sampled over more than one order of magnitude at a frequency $\omega = 0.06$ a.u. The frequency was chosen following the analysis of [48] where efficient control of the spin-transition was observed for frequencies below and above some possible

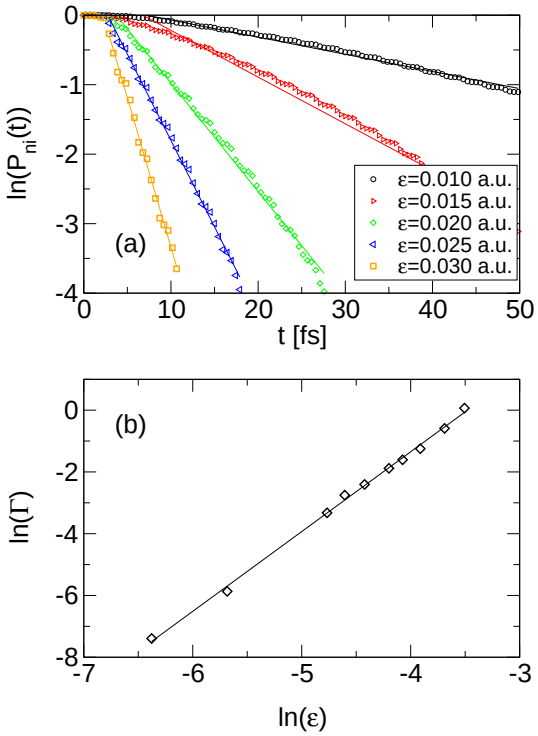


**Figure 1.** (a) Logarithmic decay of the remaining (non ionized) population $\ln(P_{ni})$ as a function of time, for different pulse amplitudes $\varepsilon$ from 0.01 to 0.03 a.u. and $\omega = 0.06$ a.u. The solid lines show the best linear fits at short times up to 100 fs. (b) Logarithmic fit of the population decay due to ionization with respect to the field amplitude giving a slope of $n = 2.6$.

one-photon electronic resonances in a simplified ESM Hamiltonian obtained by truncating the electronic basis to the first 6 Born-Oppenheimer states, disregarding ionization and non-adiabatic transitions. Then $\ln(P_{ni}) \approx -\Gamma t$ was linearly fitted to obtain the rate of ionization $\Gamma$. Fig.1 (a) shows that the linear fit is reasonably good as soon as ionization sets in, i.e., when the wave packet leaves the edges of the $3D$ grid.

In Fig.1 (b) we show the results of fitting $\Gamma$ to the field amplitude $\varepsilon$ in logarithmic scale (because we are only interested in the slope of the curves, the arguments of the logarithms are the rates in $\mathrm{fs}^{-1}$ and field strengths in a.u., respectively). With amplitudes ranging approximately from 0.002 to 0.030 a.u. the behavior is approximately linear with an exponent of $n = 2.6$. Deviations occur for lower intensities i.e. longer ionization times because the simple 2-PSI model fails to take into account the dependence of the rate with the ion's motion. However, the exponential model still provides a reasonable estimate. Power-law dependencies of the ion signal on the laser intensity with exponents between one and two are familiar from 1+1 photon resonance enhanced multiphoton ionization as studied, e.g., in the case of the NO molecule, see Ref. [52] and references therein.

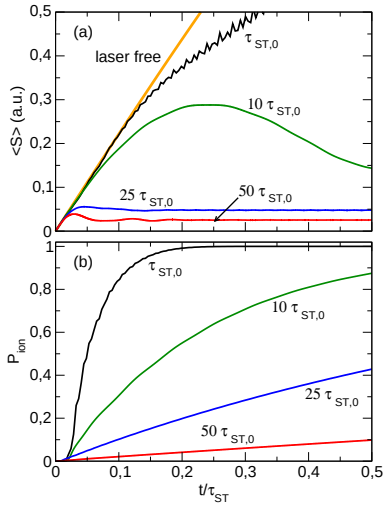


**Figure 2.** Triplet state population (a) and probability of ionization (b) as a function of the time scaled with respect to the spin-flipping time ($t/\tau_{ST}$) for different spin coupling strengths, given as multiples of a reference inverse strength $\tau_{ST,0}$. The results are obtained from the numerical solution of the time-dependent Schrödinger equation for the ESM-model and show that for $\tau_{ST} \sim 25\tau_{ST,0}$ it is already possible to control the spin transition before significant ionization occurs.

## 4. Control of spin-transfer before the onset of ionization

As shown in the previous section, $\Gamma$ can be fitted with the form given by Eq.(10) with an exponent close to but larger than 2. Thus, one expects that $\tau_{ST}$ may become smaller than $\tau_{ion}$ for weak $V_{ST}$. However, the small departure from the quadratic dependence implies that large changes in $V_{ST}$ (or correspondingly $\tau_{ST}$) will be needed to observe a shift from ionization driven to Stark-shift driven dynamics, where the spin transfer is controlled before ionization takes over.

For instance, taking the results of [47] as a reference, with $\varepsilon_0 = 0.017$ a.u. we obtained $\chi \sim 10$ (this is a rough estimation, since due to the fast ionization it is difficult to assess the decoupling between the spin states) and $\tau_{ion,0} \sim 22$ fs, which is about 6 times shorter than $\tau_{ST,0}$. With $n = 2.6$, in order to make $\tau_{ion} \sim \tau_{ST}$ while keeping $\chi$, we would need to work with a Hamiltonian with a much weaker coupling $V_{ST}$

$$\frac{V_{ST}}{V_{ST,0}} = \left(\frac{\tau_{ST}}{\tau_{ion}}\frac{\tau_{ion,0}}{\tau_{ST,0}}\right)^{2/(n-2)} \approx \left(\frac{\tau_{ion,0}}{\tau_{ST,0}}\right)^{2/(n-2)} \approx \left(\frac{1}{6}\right)^{2/n-2} \approx \frac{1}{390} \qquad (16)$$

Thus, only when the spin coupling is roughly 400 times weaker than the reference result is it possible to avoid the spin transition before substantial ionization occurs working with fields of an amplitude an order of magnitude weaker. In fact, as Eq.(9) shows, it will be possible to observe the effect on the spin decoupling before, since $\tau_e$ can be easily $3-10$ times shorter than $\tau_{ST}$.

In Fig.2 we show how the probability of ionization and the average spin angular momentum $S_{av} = \sqrt{2P_T}$ vary as a function of the scaled time ($t/\tau_{ST}$) for different choices

of the spin coupling, here written as different multiples of the reference time for the spin transition, $\tau_{ST,0}$. In the absence of an external control field, $S_{av}$ rises to $\sqrt{2}$ (not shown in the figure) while in the strong coupling case, $S_{av}$ reaches a plateau of $\sim 0.6$. The curve shows many oscillations due to numerical instabilities, as practically all population ionizes and therefore $P_{ni}$ get close to zero after $t \sim 0.2\,\tau_{ST,0} = 24$ fs. With a coupling ten times weaker ($\tau_{ST} = 10\,\tau_{ST,0}$), using a field $\varepsilon = 0.00537$ a.u. $\approx 1/\sqrt{10}\cdot\varepsilon_0$ the ionization dominates ($> 50\%$) before $\tau_{ST}$. However, as the relation of singlet to triplet state population is $\chi \sim 10$ and $\tau_e \sim \tau_{ion}$ one can observe the first attenuated coherent oscillation of $S_{av}$ before ionization takes over the system. For even weaker couplings one can clearly observe the process of spin locking with minor ionization ($< 20\%$) at times smaller or even of the order of $\tau_{ST}$. For instance, with $\tau_{ST} = 25\,\tau_{ST,0}$ we have used $\varepsilon = 0.0034$ a.u. $\approx 1/\sqrt{25}\cdot\varepsilon_0$ while for $\tau_{ST} = 50\,\tau_{ST,0}$ we used $\varepsilon = 0.0024$ a.u. $\approx 1/\sqrt{50}\cdot\varepsilon_0$. These results show that for a coupling strength of $V_{ST} \leq 1/25 \cdot V_{ST,0}$ efficient spin locking can be achieved before significant ionization occurs. The rough guess given by Eq.(16) underestimates the coupling strength required for an efficient control, but gives the right order of magnitude for convenient parameters.

## 5. Summary and Conclusion

In this work we show that spin locking with the help of external electric fields can, in principle, be achieved under certain conditions. We first analyze analyze ionization and control of spin transfer via the nonresonant dynamic Stark Effect (NRDSE) scheme in a very simple, but general, two-level approximation of a non-resonantly driven system with strong internuclear (singlet-triplet) couplings. It is found that the key feature that determines if optical spin control is possible or not is the dependence of the ionization rate on the control field amplitude. In a simple empirical model this dependence can be approximated as a power law with the exponent deciding if ionization or control is the predominant process for a given set of parameters.

The 2-PSI model reduces the electronic active states to the ground manifold (the singlet and triplet quasi-degenerate states) and lacks any nuclear dynamics. However, it can be used a guide to find suitable regimes or ranges of parameters where one can achieve the control of spin coupling in more complex systems. This requires the previous fitting of the parameters of the model with respect to the dynamics of the complex system that is being approximated.

As a numerical study, in this work we have investigated the control of the spin state in a coupled two-electron-nucleus motion under a strong field, namely the ESM Hamiltonian. It was found that the analytical estimates for the optimal values of spin coupling versus electric field strength are useful to establish an efficient quantum control of spin transitions before ionization is effective. Thus the competing processes of spin-transitions and ionization can, within certain limits, be influenced. In particular, for relatively weak spin couplings and control field intensities we could achieve efficient spin locking in an initial singlet state.

It has to be noted that our conclusions rest on the particular model (the ESM Hamiltonian) that we employ in the calculation. However, the coupled electron-nuclei model contains many essential ingredients for the description of the dynamics of molecules in laser fields. For

example, it incorporates not only the ST-coupling but also the influence of vibrational motion on the accompanying transitions being important in, e.g., biradicals which exhibit crucial ST-interactions [53]. Also, with respect to the electronic structure, the entire manifold of singlet- and triplet-states is included [47]. Within the ESM model it is possible, by a proper choice of parameters, to increase the density of electronic states which, nevertheless, is enough in the present study to allow a very efficient ionization.

Indeed, one may claim that the ESM Hamiltonian poses very challenging conditions for the control of the spin state. Namely, one observes one-photon resonant enhanced ionization and, on the other hand, the spin-coupling is very effective, as the singlet and triplet states are resonant or quasi-resonant for most nuclear geometries. Hence the nuclear dynamics does not reduce the efficiency of the singlet-triplet transition, as would be expected in other systems.

Therefore, although we emphasize the model character of the present study, we are confident that our main point, namely that it is possible to control the ST-transitions in the presence of ionization, is still valid if the dynamics of the system is more complicated, i.e., when the numbers of nuclear degrees of freedom and/or the density of electronic states increases. In each case, the spin-flip time is modified so that the field parameters have to be adjusted accordingly to achieve a successful control. To prove this definitely, much more elaborate studies are necessary which provides a challenge for the future.

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