Non-adiabatic dynamics in SO$_2$: II. The role of triplet states studied by surface-hopping simulations

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The importance of triplet states in the photorelaxation dynamics of SO$_2$ is studied by mixed quantum-classical dynamics simulations. Using the Surface Hopping including ARbitary Couplings (SHARC) method, intersystem crossing processes caused by spin-orbit coupling are found occurring on an ultrafast time scale (below 100 fs) and thus competing with internal conversion. Comparing the dynamics including singlet and triplet states to the singlet-only dynamics, very different results are obtained for the populations of the respective states. However, the vibrational motion in the triplet manifold very much resembles the one in the singlet manifold. Consequently, the contribution of the triplet states may be difficult to detect in a broad range of experiments.

I. INTRODUCTION

Sulphur dioxide is an attractive molecular system which combines a very small system size with many different excited states coupled in a complex way, offering a challenging photodynamics which can be studied with ultra-fast, time-resolved spectroscopic methods and modern high-level ab initio techniques.

In a companion paper$^1$ (hereafter referred to as paper I) the experimental and theoretical efforts of the last 80 years to characterize the electronic excited states of SO$_2$ have been surveyed in detail. Already in the 1930s$^{2,3}$ high-resolution absorption spectra of SO$_2$ were recorded. The absorption spectrum features three prominent bands in the near- and medium-UV range, named the forbidden band and the first and second allowed bands.$^4$ Especially the first allowed band between 3.6 eV and 5.1 eV was subject to numerous analyses (reviewed by Herzberg$^5$ and Heicklen et al$^6$) because of its intricate structure. From a modern point of view, this band system arises from the transition from the ground state to the vibronically coupled $^1A_2/1B_1$ system (the two lowest excited singlet states). Müller and Köppel$^7$ treated this singlet state system using full-dimensional quantum dynamics (QD) and found that the system remains primarily on the lower adiabatic potential energy surface (PES) after excitation. An extension of this study has been published very recently.$^8$

However, there is significant evidence$^{9,11}$ that the excited state dynamics within the first allowed band system is also affected by the presence of triplet states. SO$_2$ shows in the region between 3.1 eV and 3.6 eV a weak absorption profile (the forbidden band), which was shown to arise from excitation to triplet states by Douglas$^{12}$ by means of the Zeeman effect. Even though the number, location and character of the triplet states could not be determined by early spectroscopic means, modern ab initio methods showed that three states of $^3A_2$, $^3B_1$ and $^3B_2$ symmetry are present at energies slightly lower than the corresponding singlet states. Consequently, intersystem crossing (ISC) between singlet and triplet states could be plausible and the photodynamics of SO$_2$ might be influenced by both ISC and internal conversion (IC) processes.

Very recently, both spectroscopic$^{13-18}$ and theoretical$^{19,20}$ studies suggested that in a number of systems ISC indeed can compete with IC on an ultrafast time scale. In order to provide more evidence for these new findings, several experimental methods based on high-resolution time-resolved spectroscopy have been developed.$^{22,23}$ Further experimental indications for the case of SO$_2$ can be found in paper I.

In the present paper, we attempt to unravel the excited state dynamics of SO$_2$ theoretically. To this aim, ab initio surface hopping molecular dynamics (MD) is employed using the SHARC code.$^{29}$ SHARC (Surface Hopping including ARbitary Couplings) can treat IC and ISC, mediated by non-adiabatic couplings and spin-orbit couplings, respectively, on the same footing. This is achieved by performing surface hopping in a basis of spin-orbit-coupled electronic states, which are obtained by diagonalization of the potential energy matrix including the spin-orbit couplings. The simulations are focused on the energy range corresponding to the forbidden and first allowed band of the experimental absorption spectrum.$^{30}$ The applicability of SHARC on SO$_2$ is validated by running also trajectories on the singlet-manifold only, whose results are compared with those obtained by Müller and Köppel using accurate quantum dynamical (QD) calculations.$^5$ Other applications of SHARC can be found in Refs. 29, 31, 33.

II. METHODOLOGY

In the following, a brief summary of general surface hopping method as well as the specific SHARC variant is given. Further details on SHARC can be found in Ref. 29. A summary of the employed ab-initio methods and initial
conditions generation is also given below.

A. Surface hopping

The widely applied fewest switches criterion for surface hopping was devised by Tully in 1990.\cite{34} It allows incorporating non-adiabatic effects into semi-classical ab initio dynamics,\cite{35} where the nuclei can be propagated on only one PES at a time, by means of state hops according to jumping probabilities. To this end, the electronic wavefunction is expanded in the basis of adiabatic eigenstates $|\psi_{\alpha}\rangle$ of the Hamiltonian:

$$ |\psi\rangle = \sum_{\alpha} c_{\alpha} |\psi_{\alpha}\rangle. \quad (1) $$

The state coefficients $c_{\alpha}$ are obtained by numerical integration of the time-dependent Schrödinger equation:

$$ \frac{\partial}{\partial t} c_{\beta} = - \sum_{\alpha} c_{\alpha} [i\delta_{\beta\alpha} E_{\alpha} + \mathbf{v} \cdot \mathbf{T}_{\beta\alpha}], \quad (2) $$

where $\mathbf{v}$ is the velocity vector, $E_{\alpha}$ is the adiabatic energy of state $\alpha$ and

$$ \mathbf{T}_{\beta\alpha} = \langle \psi_{\beta} | \nabla \mathbf{r} | \psi_{\alpha}\rangle \quad (3) $$

is the non-adiabatic coupling vector.

Based on the state coefficients, the hopping probabilities from the current state into any other state can be computed according to:

$$ P_{\beta\to\alpha} = \frac{2\Delta t}{c_{\beta}^2 c_{\alpha}^2} \Re \left( c_{\beta}^* c_{\alpha} [iH_{\beta\alpha} + \mathbf{v} \cdot \mathbf{T}_{\beta\alpha}] \right). \quad (4) $$

B. Surface hopping including arbitrary couplings

In the scheme outlined above, the electronic Hamiltonian was assumed to be diagonal in the basis of the wavefunctions $|\psi_{\alpha}\rangle$. If perturbation terms are added to the Hamiltonian, off-diagonal elements between the states under consideration may be introduced:

$$ H_{\beta\alpha}^{(1)} = H_{\beta\alpha}^{(0)} + \langle \psi_{\beta}^{(0)} | \tilde{H}^{(1)} | \psi_{\alpha}^{(0)} \rangle. \quad (5) $$

Such perturbations include for example spin-orbit coupling, but also the interaction with laser fields. Within the SHARC algorithm, the Hamiltonian $H_{\beta\alpha}^{(1)}$ is diagonalized by an unitary transformation. To obtain a consistent adiabatic picture, the non-adiabatic couplings are transformed into the new basis $\{|\psi_{\beta}^{(1)}\rangle\}$ according to:

$$ \mathbf{T}_{\beta\alpha}^{(1)} = \left( \mathbf{U}^{\dagger} \mathbf{T}^{(0)} \mathbf{U} \right)_{\beta\alpha}, \quad (6) $$

so that the final equation for the evolution of the state coefficients is

$$ \frac{\partial}{\partial t} c_{\beta} = - \sum_{\alpha} c_{\alpha} \left[ i \left( \mathbf{U}^{\dagger} \mathbf{H} \mathbf{U} \right)_{\beta\alpha} + \mathbf{v} \cdot \left( \mathbf{U}^{\dagger} \nabla \mathbf{U} \right)_{\beta\alpha} \right], \quad (7) $$

The motion of the nuclei is governed by gradients obtained numerically from the unperturbed gradients under the approximation of constant spin-orbit coupling elements, which is a good approximation as long as the coupling elements or their change are small. To date no analytical gradients for spin-orbit-perturbed states are available, but work is in progress.\cite{39}

Using the described unitary transformation, the obtained states are not spin-pure states anymore because singlets and triplets mix via spin-orbit coupling. However, in the basis of spin-orbit-coupled electronic states, IC and ISC are not fundamentally different anymore and can be conveniently investigated using non-adiabatic dynamics.

C. Ab initio methods

Throughout this paper, the nuclear motion of SO$_2$ is discussed in terms of a set of internal coordinates consisting of the average bond length, $r_{\text{sym}}$, one half of the bond length difference, $r_{\text{asym}}$, and the bond angle, $\theta$:

$$ r_{\text{sym}} = \frac{1}{2}(r_1 + r_2), \quad r_{\text{asym}} = \frac{1}{2}(r_1 - r_2), \quad (8) $$

where $r_1$, $r_2$ and $\theta$ are defined in figure 1. The MD calculations themselves were carried out in cartesian coordinates.

The on-the-fly electronic structure calculations required for the MD simulations were performed with the MOLPRO 2010.1 package\cite{38} which was interfaced to SHARC. In order to achieve a description of the
A. State terminology

To compare theoretical results to experimental findings, a note on nomenclature is in order, since spectroscopic results are usually discussed in terms of diabatic states (where the wavefunction character is preserved), while ab initio MD simulations typically employ adiabatic states (where the potential coupling between states vanishes) \[\text{III. RESULTS}\]

E. Initial conditions

The generation of the initial geometries and velocities was carried out with the Newton-X program suite. A quantum harmonic oscillator Wigner distribution was generated using numerical frequencies obtained with RI-MP2 and the basis set cc-pVTZ, as implemented in the TURBOMOLE 6.2 suite.

The obtained initial conditions displayed bond lengths between 1.36 Å and 1.54 Å and bond angles between 110° and 128°. The initial kinetic energies showed an average of 0.09 eV, with a maximum of 0.5 eV.

All trajectories started in one of the excited states at \(t=0\), which is equivalent to a delta pulse excitation. The initially populated state was determined stochastically as \(\theta = 0\), which is equivalent to a delta pulse excitation. The state coefficient of state \(c_\alpha\) was set equal to 1 and \(c_\beta \neq c_\alpha\) equal to 0.

III. RESULTS

A. State terminology

To compare theoretical results to experimental findings, a note on nomenclature is in order, since spectroscopic results are usually discussed in terms of diabatic states (where the wavefunction character is preserved), while ab initio MD simulations typically employ adiabatic states (where the potential coupling between states vanishes). Experimentally, the PES are shown in the \((r_{\text{asym}}, \theta)\) space. \(\text{SO}_2\) exhibits \(C_{2v}\) symmetry if \(r_{\text{asym}} = 0\); otherwise, the point
FIG. 2. PESs of (a) singlet states $S_1$ (lower surface) and $S_2$ (upper surface) and (b) of triplet states $T_1$ (lowest), $T_2$ (intermediate), and $T_3$ (highest). Colors indicate the wavefunction character of the adiabatic states, where purple corresponds to $1^1A_2$ or $1^3A_2$, cyan to $1^1B_1$ or $1^3B_1$ and green to $1^3B_2$. For $r_{asym} \neq 0$, the dominating character is indicated by red ($A_2$), blue ($B_1$) or grey (mixed).

The same color scheme is used for the triplet states, shown in figure 2(b). Additionally, the state $1^3B_2/1^3A'$ is shown in green. Since even in $C_s$ symmetry this state does not mix with the $A''$ states, it retains its wavefunction character along the whole surface. The adiabatic triplet states used in the MD simulations are called $T_1$, $T_2$ and $T_3$ and are obtained from $1^3A''$, $2^3A''$ and $1^3A'$ by ordering the states strictly according to the energy at each geometry. For example, the $T_2$ consists of the visible part of the green surface and the lower cone (pointing upwards) situated energetically above the green surface.
In figure 3, panels (a) and (b) depict the potentials in figure 2 but using different axis ranges. In panel (a), $r_{\text{sym}}=1.5$ Å, which is similar to $r_{\text{sym}}$ at the ground state equilibrium geometry. The ground state energy is given as a greyscale contour to indicate the Franck-Condon region. In panel (b), $r_{\text{sym}}=1.7$ Å, which exemplarily represents the more stretched geometries found during the course of the MD simulation (see below). Regions of strong non-adiabatic coupling between the singlet states are shaded in dark blue, while yellow indicates regions where triplets are close to singlet states (less than 0.05 eV $\approx 400$ cm$^{-1}$). In panels (c) and (d), the potentials of the three lowest-lying triplet states are shown analogously.

In both panels (a) and (b), the singlet states are connected via a conical intersection (CI) directly situated above the Franck-Condon region (in (a) at $\theta=118.5^\circ$ and $r_{\text{asym}}=0.0$ Å; in (b) at $\theta=120.0^\circ$ and also $r_{\text{asym}}=0.0$ Å). The $S_2$ surface forms a narrow funnel without any intersection with triplet states. In contrast, the $S_1$ intersects with all three triplet states. Close to the CI, the $S_1$ crosses with the $T_3$, while $T_1$ and $T_2$ come close for larger values of $r_{\text{asym}}$. At large values for $r_{\text{sym}}$, the $S_1$ surface exhibits a double-minimum (see panel (b)).

Since the triplet states have basically the same wavefunction character as their corresponding singlet states, the PESs are very similar. In panel (c), the $T_2/T_3$ CI is located at $\theta=111.0^\circ$, $r_{\text{asym}}=0.0$ Å and in panel (d) at $\theta=113.5^\circ$, $r_{\text{asym}}=0.0$ Å.

### C. Spectrum

Using the excitation energies $E_{0\alpha,j}$ and the dipole moments $\mu_{0\alpha,j}$ of the initial geometries of all trajectories $j$ for all states $\alpha$, an approximation to the absorption spectrum has been simulated via a Gaussian convolution:

$$g_{\alpha}(E) = \sum_{j} f_{0\alpha,j} \cdot \exp \left( -\frac{(E - E_{0\alpha,j})^2}{2\epsilon^2} \right).$$

Here, $g_{\alpha}(E)$ is the part of the absorption spectrum arising from the transition from the ground state to state $\alpha$, depending on the energy $E$. The parameter $\epsilon=0.027$ eV describes the width of the Gaussian broadening. The spectrum is based on the properties of 280 initial conditions.

The total absorption spectrum is the sum of $g_{\alpha}(E)$ over all states $\alpha$. To account for the first allowed band of SO$_2$, only the two adiabatic states $S_1$ and $S_2$ need to be considered. The obtained total spectrum together with its contributions from the transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$, as well as the experimental spectrum, are depicted in figure 4. Both spectra were normalized. The agreement between theory and experiment is satisfactory, considering the overall energy range and the general shape of the band, although the calculated spectrum is slightly redshifted. The shape of the high-energy flank of the spectrum is well reproduced, while the low-energy flank gives too high oscillator strengths for energies below 3.9 eV. Naturally, the vibrational structure of the spectrum cannot be reproduced by this semi-classical method.

### D. Dynamics in the singlet-manifold

In order to validate our method, we first performed a simulation of an ensemble of 42 trajectories, including only the three lowest-lying singlet states $S_0$ to $S_2$. Thus, the results are directly comparable to those obtained by Müller and Köppel by using full-dimensional QD on pre-calculated PESs for $S_1$ and $S_2$. The PESs used in their simulations were obtained from the earlier work of Weis.

Figure 5 also depicts the time-dependent populations of $S_1$ and $S_2$ as obtained by Müller and Köppel (grey curves). At $t=0$, both states are populated, but $S_1$ absorbs a larger fraction of the population. During the first femtoseconds, some small population fluctuations take place. After approximately 10 fs, the $S_2$ starts to transfer population to the $S_1$ and gets completely depopulated after 40 fs. After about 65 fs, again some population is transferred from $S_1$ to $S_2$, because the wavepacket/ensemble returns to the interaction region of $S_1$ and $S_2$ near the Franck-Condon point.

Figure 5 also depicts the time evolution of $S_1$ and $S_2$ obtained with SHARC. As it can be seen, the initial population ratio obtained with SHARC is comparable to that predicted by QD. In the MD simulation, however, the population transfer from $S_1$ to $S_2$ is faster (during the first 5 fs). Starting at about 15 fs, the $S_2$ begins to continuously transfer population to the $S_1$ until the former...
is completely depleted at around 60 fs. Between 70 and 80 fs the $S_2$ is repopulated, slightly delayed compared to the results of Müller and Köppel. By the end of the propagations (100 fs), both methods predict a similar population exchange between both electronic states. In summary, despite different levels of theory in the QD and the MD simulations, a satisfactory agreement is found between both methods.

**E. Dynamics in the singlet-triplet manifold**

Encouraged by the general agreement found in the dynamics performed within the singlet-manifold, an ensemble of 207 trajectories (171 starting in $S_1$ and 36 in $S_2$) was propagated for 800 fs, now allowing the interaction with triplet states. In the following analysis, special emphasis is put on the first 100 fs of the simulation.

Figure 5 displays the relative populations of all singlet and triplet states depending on time in logarithmic scale. For simplicity, the populations of the three $M_5$ components of each triplet state were summed up. The colors denoting the states in figure 6 (singlet states in shades of blue, triplets in shades of red) are used consistently in all subsequent figures to allow for quick recognition of the respective state.

In accordance with dynamics on the singlet-manifold, the initial population ratio is approximately 0.8:0.2 for $S_1:S_2$. The triplet states are unpopulated initially (note that figure 6 starts at $t=1$ fs). However, the course of the dynamics shows remarkable differences with respect to the singlet-only case. Already after less than 10 fs, the population of $S_1$ and – to a lesser extent – $S_2$ decreases, while the one of $T_3$ increases. The lower-lying $T_1$ and $T_2$ are populated only after around 30 fs. At the same time, the population of $S_1$ is diminished substantially. For later times, the states’ populations fluctuate around some mean value: $S_1$ keeps about 50% of the total population, $T_1$ and $T_2$ keep 20% each, and $S_2$ and $T_3$ the remainder. During the course of the simulation, also a small number of trajectories relaxed to the ground state $S_0$.

In order to obtain a detailed interpretation of the state interactions, the numbers of trajectories hopping from state $\beta$ to state $\alpha$ at time step $t_n$, denoted $\Delta N_{\beta \alpha}(t_n)$, are analyzed. We use a Gaussian convolution in order to convert the discrete $\Delta N_{\beta \alpha}(t_n)$ into more comprehensible, continuous data. The obtained “density of state hops” at time $t$ is

$$N_{\beta \alpha}(t) = \sum_n \Delta N_{\beta \alpha}(t_n) \cdot \exp\left(-\frac{(t_n - t)^2}{2\tau^2}\right),$$  

(14)

with a broadening parameter of $\tau=5$ fs. In the data so depicted, the area under the curves of $N_{\beta \alpha}(t)$ is proportional to the number of state hops in a given time interval. The density of state hops is given in figure 7 for the first 300 fs.

Additionally, in order to extract time constants for the population transfer rate, we cumulate the number of state hops and fit all early transfer events separately using exponentials and all later ($>100$ fs) according to zero-order kinetics (for an explanation of this distinction between early and late events, see below).

Figure 7 shows the interaction of $S_2$ with $S_1$. Directly after the start of the simulation and again after approximately 35 fs, $S_2$ transfers population to $S_1$. For later times, $S_2$ does not show notable interaction with $S_1$. The fitting procedure gave time constants of 7 and 8 fs, respectively, for the two transfer events. Combined, 16% of all trajectories were transferred to $S_1$.

$T_1$ gets populated from $S_1$ (panel (b)) after 30 fs and immediately afterwards the same amount of population is transferred back (boxes (2) and (3)). Consequently, during the first 100 fs, no net transfer from $S_1$ to $T_1$ is observed.

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**FIG. 5.** Relative population of $S_1$ and $S_2$ in the QD simulation of Müller and Köppel (black and grey) and the corresponding results of an MD simulation including 42 trajectories (blue). Data taken from their paper.[10]

**FIG. 6.** Relative population of the six states in the dynamics simulation including triplet states.
After 20 fs, \(S_1\) transfers a large number of trajectories to \(T_2\) (panel (c), box (4)) and again after 40 fs (box (5)). Treating the interval from 20 fs to 100 fs as one event, an effective time constant of 13 fs and a total transfer of 33% of all trajectories is found.

The interaction between states \(S_1\) and \(T_3\) in panel (d) provides the earliest ISC process. The transfer of population to \(T_3\) (box (6)) starts immediately and during the first 100 fs, about 15% of all trajectories switch to \(T_3\) with an effective time constant of 8 fs.

The states \(T_1\) and \(T_2\) also interact with each other, see panel (e). Box (7) shows a transfer from \(T_2\) to \(T_1\), starting after 20 fs. The exponential fit of the cumulated net hops yields a time constant of 11 fs.

The last pair of states exhibiting notable interactions is \(T_2\) and \(T_3\), which are connected via a CI similar to the one linking \(S_2\) and \(S_1\). Panel (f) of figure 7 shows that the CI facilitates the ultrafast decay from \(T_3\) to \(T_2\) as soon as \(T_3\) is populated. This process is slightly slower than the ones already mentioned, with an estimated time constant of 17 fs.

The state interactions for later times than 100 fs exhibit characteristics very different from the early part of the simulation. \(S_2\) and \(T_1\) interact significantly less with \(S_1\). However, states \(S_1\), \(T_2\) and \(T_3\) exchange population in a circular fashion, shown in the three boxes labeled (9). This cycle consists of three steps, \(T_2 \rightarrow S_1\) in panel (c), \(S_1 \rightarrow T_3\) in panel (d) and \(T_3 \rightarrow T_2\) in panel (f). The cumulated net hops of these three interactions for times greater than 100 fs were fitted according to zero-order kinetics. Time constants of 10, 13 and again 13%/100 fs (% of all trajectories per 100 fs) were found, respectively.

Figure 8 shows the evolution of the internal coordinates of all trajectories in all states. In panel (a), the dynamics in the asymmetric stretch mode is depicted. The lower-lying excited states \(S_1\), \(T_1\) and \(T_2\) all show a strong excitation of this mode. \(T_2\) and \(T_1\) get only populated once the \(S_1\) trajectories has moved to large enough values of \(r_{\text{asym}}\). All three states show almost exactly the same motion with regards to oscillation period and amplitude, thus we define these states as one group in the following discussion. On the contrary, a very different kind of motion is exhibited by \(S_2\) and \(T_3\), which do not show any excitation of the asymmetric stretch mode. These two states therefore are classified as a second group.

The classification of the excited states into the groups \(S_1\), \(T_1\) and \(T_2\) on the one hand and \(S_2\) and \(T_3\) on the other hand is confirmed by the other modes. For the symmetric stretch mode in panel (b), an oscillation period of 70 fs and maximum \(r_{\text{sym}}\) of 1.8 Å is found for the first group, while the second group performs one oscillation in 45 fs with a maximum \(r_{\text{sym}}\) of slightly above 1.7 Å. The bending mode (panel (c)) of \(S_1\), \(T_1\) and \(T_2\) show a period of 70 fs and a minimum angle of 95°, the values of \(S_2\) and \(T_3\) are 45 fs and 105°.

IV. DISCUSSION

A. Potential energy surfaces

The excitation in \(SO_2\) takes place from the \(1^1A_1\) ground state to the bright \(1^1B_1\) state. In the Franck-Condon region, this state crosses with \(1^1A_2\) and gives rise to a CI. Thus, in our adiabatic picture (see subsection III A) the bright state \(1^1B_1\) contributes to both \(S_1\) and \(S_2\) (for \(\theta < 118.5^\circ\) mainly \(S_2\), otherwise mainly \(S_1\)) and consequently both \(S_1\) and \(S_2\) are populated by the initial delta pulse. Because the CI is located right at the Franck-Condon region, IC takes place immediately after excitation. Another interesting feature of the PESs is the location of singlet-triplet interaction regions, favoring ISC (see figure 8). Firstly, the intersection of \(S_1\) and \(T_3\) circularly surrounds the \(S_2/S_1\) CI and the Franck-Condon region. Therefore, all trajectories leaving the Franck-Condon region are forced to pass through this intersection. There, the spin-orbit coupling elements are on the order of 30 cm\(^{-1}\) and thus able to transfer a re-
markably large number of trajectories to the triplet PES. Secondly, the regions of proximity of \( S_1 \) and both \( T_1 \) and \( T_2 \) coincide with the outer turning point of the \( S_1 \) asymmetric stretch mode, see Figure 8 (b). Since at the turning point the potential is rather flat, the trajectories spend a long time in this region after excitation of the asymmetric stretch mode. Also in this region the spin-orbit couplings amount to about 30 cm\(^{-1}\) and allow for a noteworthy ISC yield. Since in this part of the PES \( S_1 \), \( T_1 \) and \( T_2 \) all become very close in energy, simultaneous ISC to \( T_1 \) and \( T_2 \) becomes possible.

### B. Spectrum

As can be seen in Figure 3, both transitions \( S_0 \rightarrow S_1 \) and \( S_0 \rightarrow S_2 \) contribute to the spectrum to a similar extent. The resulting calculated absorption spectrum is in reasonable agreement with the experimental one, although small deviations are patent. First, the calculated overall band shape is slightly red-shifted, by approximately 0.1 eV. This may be attributed to the double-zeta quality of the basis set since preliminary calculations indicate that larger basis sets give slightly higher excitation energies for all considered excited states. Despite its lesser accuracy, the double-zeta basis set was employed for the sake of computational performance during the dynamics.

Second, while the high-energy slopes of both spectra are quite similar, the low-energy slope of the calculated spectrum features too high intensities. In the experimental spectrum, at around 3.8 eV the absorption is already close to zero, while in the calculated spectrum the slope extends until 3.5 eV. It is noteworthy that the experimental 0-0 transition for this band has been located at around 3.46 eV \(^{[23]}\), so the obtained excitation energies are plausible and only the intensities are overestimated.

Finally, it is obvious that the vibrational structure of the spectrum is not reproduced by our simulation. A description of this phenomenon goes beyond the scope of this work, since it requires a quantum-mechanical treatment of the nuclear motion. A semi-classical simulation cannot account for quantization of the vibrational energy levels and also is not able to deliver nuclear wavefunction overlaps, which are necessary to obtain Franck-Condon factors. Thus, a correct calculation of the total absorption is not possible within this approach. The absence of the Franck-Condon factors might also explain the too intense low-energy slope in the calculated spectrum.

In conclusion, given the employed theoretical model, the simulated spectrum is in good agreement with the experiment and confirms the correctness of the initial conditions.

### C. Dynamics in the singlet-manifold

A good agreement is obtained between the QD simulation by Müller and Köppel \(^{[6]}\) and our singlet-only MD simulations (recall Figure 6). Right after excitation, the states \( S_1 \) and \( S_2 \) briefly interact while still in proximity to the CI. However, already after ca 10 fs the population on \( S_1 \) has moved sufficiently far away from the CI to cease \( S_1 \rightarrow S_2 \) population transfer. Afterwards, only the \( S_2 \) population stays close to the interaction region, since the cone focusses the population on the intersec-
tion. Consequently, between 10 fs and 60 fs a decay from $S_2$ to $S_1$ is found. At 60 fs, the $S_2$ surface is completely depopulated in both QD and MD simulations.

The use of CASSCF in the QD simulation and of MRCI in the MD simulation lead to differences in the potentials’ slopes, non-adiabatic coupling strengths and the exact location of the CI. Already Katagiri et al.\textsuperscript{23} noticed that the CASSCF method gives unsatisfactorily flat potentials of the $S_1$ state near the O–S–O dissociation limit. On the contrary, the dissociation energy as obtained on the MRCI level of theory (about 5.8 eV) is very close to the experimental one at 5.65 eV. The small discrepancies in the populations of the two simulations can be explained in this way.

After 70 fs (QD) or 80 fs (MD), the population on the $S_1$ surface returns to the $S_1/S_2$ intersection area in the Franck-Condon region. At this point, the $S_2$ is partly repopulated, though the initial population is not reached in both simulation types. This is reasonable in the sense that the ensemble already exhibits a considerable spread and the CI is missed by part of the ensemble.

In both studies, the wavepacket/ensemble basically moves all the time in $S_1$, despite having sufficient energy to reach the $S_2$. This behaviour can be attributed to the wavepacket/ensemble avoiding the CI because of the surrounding double-minimum potential (see figure 3). Following the potential energy gradient, the wavepacket/ensemble moves into regions of $r_1 \neq r_2$, where the two surfaces avoid each other and the non-adiabatic coupling is small. Also, both studies show that for times after 80 fs a coherent motion is virtually lost. Note that the experiment (see paper I) indicates a long-lived coherent motion. Although we could only speculate about the reasons for this disagreement in the QD case, we attribute the discrepancies between experiment and our MD results to our approximate MRCI gradients (see section II D). We are aware of the shortcomings of these gradients, however, MRCI potentials are necessary to qualitatively the SO$_2$ dynamics and these gradients are the best approximation currently available compatible with the SHARC methodology.

To sum up the findings so far, it is shown that the semi-classical dynamics gives results in satisfying agreement with the quantum dynamical results of Müller and Köppel. Both show a high population of $S_1$ at all times, with a fraction of the population oscillating between the two surfaces.

D. Dynamics in the singlet-triplet manifold

One of the most important results of this study is that the inclusion of triplet states leads to a completely different picture than that obtained in the singlet-only dynamics. ISC plays a significant role in the deactivation of SO$_2$ and, as can be seen from figure 6 (d) ISC even competes with IC on a timescale of tens of femtoseconds. Experimental results of paper I (figure 6 (d)) also hint at the participation of ISC in the ultrafast dynamics of SO$_2$.

The differences between the singlet-only and the singlet-triplet dynamics are discussed in detail in the following. Already during the first 5 fs, in the singlet-only dynamics there is considerable population transfer between $S_1$ and $S_2$ close to the CI, while in the singlet-triplet simulation this exchange is almost absent. Instead, the $S_1$ population approaches the intersection with $T_3$ very fast and a large number of trajectories hop to the triplet surface.

The presence of $T_3$ also governs the fate of $S_2$ at later times. In the singlet-only simulation, $S_2$ is repopulated each time $S_1$ returns to the Franck-Condon region since the $S_2/S_1$ CI located there. In the singlet-triplet simulation, the $S_1/T_3$ intersection completely surrounds the CI and all trajectories returning to the Franck-Condon region have to pass through the singlet-triplet intersection. This leads to $T_3$ scavenging a large amount of incoming trajectories which could otherwise repopulate $S_2$. It is mainly this mechanism which prevents $S_2$ from contributing significantly at later times.

However, the inclusion of the triplet states has its greatest impact on the dynamics on $S_1$. This state acts as the central hub in the dynamics and directly interacts with all other excited states under consideration. Therefore, in contrast to the singlet-only case, the $S_1$ is heavily depleted by ISC. The large number of trajectories showing ISC can be rationalized by the fact that the $S_1$ interacts with the triplets over a wide range of geometries, while the singlet-singlet interaction is significant only in a very localized area (the CI).

The analysis of the net hops between the surfaces, presented in Figure 7, and the description of the photorelaxation scheme (Figure 8) that collects the processes encountered in the photorelaxation dynamics of SO$_2$. Each state is represented by a box, indicating also its respective initial population. The $S_0$ is absent from the figure, since relaxation to the ground state is unlikely in the time scales we are considering here.

The population transfer events have been divided into two sets. In the first set – the early transfers happening during the first 100 fs – mostly temporally localized events occur (solid arrows in the figure), while for later times we see the continuous population transfers (dashed arrows) of the second set. The temporal localization is caused by the trajectories moving collectively and passing jointly through the different interaction regions. For each localized transfer event, the effective time constant $\tau$, the onset of this process and the percentage of the total population transferred in this event is given next to the corresponding solid arrow. Only major events are indicated. It is immediately obvious that $S_1$ interacts with all other excited states. It can also be seen that ISC and IC start instantly and consequently, both mechanisms act on an ultrafast timescale.

After approximately 100 fs, the ensemble of trajectories is considerably spread across the surfaces and therefore temporally localized events are not observed any-
In states $S_1$, $T_1$, and $T_2$, some trajectories show asymmetric stretch oscillations (figure 8 (a)) exclusively in one of the wells of the double-minimum potential (from $r_{\text{asym}}=0.0$ to around $0.4$ Å and back) with a period of about 70 fs. Another portion of the ensemble overcomes the central barrier and oscillates in both wells (from $r_{\text{asym}}=-0.4$ to $+0.4$ Å), with a full-cycle period of 140 fs. Interestingly, the oscillation period of 70 fs is also found in the symmetric stretch and bending modes (figure 8 (b) and (c)). Accordingly, the ensemble returns to the Franck-Condon region after this time interval and similarly at multiples of 70 fs.

From the spacing of the Clement’s bands in the absorption spectrum (approximately 28 meV) one would expect a recurrence time of 148 fs. This time coincides with the asymmetric oscillation period across both potential wells found in the simulation, but is about double the first recurrence time of the ensemble in the Franck-Condon region. Our recurrence time of about 70 fs would lead to a spacing of 59 meV, which could in principle be hidden under the peaks spaced by 28 meV. In order to recover the relative experimental peak heights in the spectrum, the second recurrence needs to be more pronounced than the first one. We do not observe such a behavior. The reason is possibly that the ensemble is already too strongly dispersed prior to the second recurrence due to our approximate gradients. We believe that the oscillation period of 70 fs is correct, but is only due to a partial recurrence to the Franck-Condon region. Consequently, the expected peaks in the TRPEPICO (time-resolved photoelectron photoion coincidence) spectra of paper I might be hidden under the peaks corresponding to the 140 fs period. The full recurrence after these 140 fs is underestimated in our dynamics most probably because of the approximate gradients. Our rationale is supported by the findings of Leveque et al. published very recently. In their remarkable study, they discuss the role of the different spectroscopic states in detail and are able to achieve almost quantitative agreement with the experimental spectrum for the first time.

**V. CONCLUSION**

This work is – to the best of our knowledge – the first ab initio-based dynamics study to investigate the singlet-triplet interactions in sulphur dioxide. The comparison with singlet-only results from QD and ab initio MD reveals that the inclusion of the triplet states is essential in order to understand the photodynamics of this system. Due to the presence of singlet-triplet intersections at accessible sites on the PESs, not only ultrafast ISC processes have been found, but those strongly influence the singlet-singlet interaction.

After the initial delta pulse excitation, 80% of all trajectories start in the $S_1$ state and 20% in $S_2$. While $S_2$ quickly decays to $S_1$ via a $S_2/S_1$ CI, in $S_1$ the asymmetric stretch mode is strongly excited. This stretch-
ing of the S–O bonds leads the trajectories inevitably through the intersection regions $S_1/T_1$ and slightly later $S_1/T_1/T_2$. Spin-orbit couplings on the order of 30 cm$^{-1}$ are responsible for an efficient and ultrafast ISC in the regions of near-degeneracy. ISC together with IC between the triplet states is responsible for an efficient and ultrafast ISC in the reaction.

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Weis used SA5-CASSCF(18,12) for the calculations. A contraction of the (18s,13p) basis set of Partridge (NASA Technical Referendum 89449 (1987)) with additional d, f and diffuse s and p functions was employed for sulphur. For oxygen, a contraction of the basis of van Duijneveldt (IBM Research Report RJ945 (1971)) with polarization functions of Dunning (J. Chem. Phys. 90, 1007 (1989)) was used. Weis diabatized the obtained potentials of $S_1$ and $S_2$ in a way that the transition dipole moment between the ground state and one of the two excited states becomes minimal. In the end, these diabatic potentials and the off-diagonal element $V_{12}$ were fitted analytically, where $V_{12} = \frac{1}{2} \lambda (r_1 - r_2)$ was used.

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