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Electronic Supporting Information for

Highly efficient surface hopping dynamics using a linear vibronic coupling model

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LVC Parameters

Table S1: LVC-Parameters (eV) for SO_2 computed at the MR-CIS(6,6)/ANO-RCC-VDZP level of theory.[a]

	ϵ_n	$\kappa^{(n)}_{1a_1}$	$\kappa^{(n)}_{2a_1}$	$\lambda^{(mn)}_{b_2}$	
$^1A_1$	0	0	0	$^1A_1/^1B_2$	-0.498472
$^1B_1$	4.462792	0.032558	0.331565	$^1B_1/^1A_2$	0.199193
$^1A_2$	4.847730	-0.217356	0.504755		
$^1B_2$	6.805345	-0.121284	0.482766		
$^3B_1$	3.649723	0.078288	0.222898	$^3B_1/^3A_2$	0.155580
$^3B_2$	4.478220	-0.136967	0.499509		
$^3A_2$	4.627331	-0.219168	0.506301		

[a] The frequencies are: $\omega_{1a_1} = 518.75\text{cm}^{-1}$, $\omega_{1a_2} = 1165.17\text{cm}^{-1}$, $\omega_{1a_1} = 1405.24\text{cm}^{-1}$.

Table S2: LVC-Parameters (eV) for SO_2 computed at the MR-CISD(12,9)/ANO-RCC-VTZP level of theory.[a,b]

	ϵ_n	$\kappa^{(n)}_{1a_1}$	$\kappa^{(n)}_{2a_1}$	$\lambda^{(mn)}_{b_2}$	
$^1A_1$		-0.017641	-0.024908	$^1A_1/^1B_2$	0.451491
$^1B_1$	4.226686	0.028991	0.294386	$^1B_1/^1A_2$	-0.151271
$^1A_2$	4.595060	-0.215731	0.444536		
$^1B_2$	8.403901	-0.130622	0.463663		
$^3B_1$	3.349913	0.070993	0.189128	$^3B_1/^3A_2$	-0.099622
$^3B_2$	4.210887	-0.142804	0.465614		
$^3A_2$	4.356258	-0.217377	0.440914		

[a] The frequencies are: $\omega_{1a_1} = 518.75\text{cm}^{-1}$, $\omega_{1a_2} = 1165.17\text{cm}^{-1}$, $\omega_{1a_1} = 1405.24\text{cm}^{-1}$.
[b] Reference geometry and vibrations determined at the MR-CIS level. Therefore, the κ values for the ground state do not vanish.

Table S3: Diabatic spin-orbit coupling parameters η_{mn} (cm^{-1}) of SO_2 determined at the MR-CIS(6,6)/ANO-RCC-VDZP level of theory.

	$^3B_1(0)$	$^3B_2(0)$	$^3A_2(0)$	$^3B_1(+)$	$^3B_2(+)$	$^3A_2(+)$	$^3B_1(-)$	$^3B_2(-)$	$^3A_2(-)$
$^1A_1$	0.00	0.00	-34.96	134.35	0.00	0.00	0.00	1.04	0.00
$^1B_1$	0.00	-23.83	0.00	0.00	0.00	0.00	0.00	0.00	-52.02
$^1A_2$	0.00	0.00	0.00	0.00	-48.03	0.00	48.02	0.00	0.00
$^1B_2$	6.69	0.00	0.01	-0.01	0.00	-65.74	0.00	0.00	0.00
$^3B_1(0)$	0.00	0.00	0.00	0.00	0.00	-49.62	0.00	0.00	0.00
$^3B_2(0)$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-52.71
$^3A_2(0)$	0.00	0.00	0.00	49.62	0.00	0.00	0.00	52.71	0.00
$^3B_1(+)$	0.00	0.00	49.62	0.00	0.00	0.00	0.00	-17.69	0.00
$^3B_2(+)$	0.00	0.00	0.00	0.00	0.00	0.00	17.69	0.00	0.00
$^3A_2(+)$	-49.62	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$^3B_1(-)$	0.00	0.00	0.00	0.00	17.69	0.00	0.00	0.00	0.00
$^3B_2(-)$	0.00	0.00	52.71	-17.69	0.00	0.00	0.00	0.00	0.00
$^3A_2(-)$	0.00	-52.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table S4: Diabatic spin-orbit coupling parameters η_{mn} (cm^{-1}) of SO_2 determined at the MR-CISD(12,9)/ANO-RCC-VDZP level of theory.

	$^3B_1(0)$	$^3B_2(0)$	$^3A_2(0)$	$^3B_1(+)$	$^3B_2(+)$	$^3A_2(+)$	$^3B_1(-)$	$^3B_2(-)$	$^3A_2(-)$
$^1A_1$	0.00	-0.03	-45.87	-146.25	0.00	0.03	0.00	-0.45	0.01
$^1B_1$	0.00	26.93	-0.01	0.00	-0.02	0.00	-0.02	-0.01	-54.90
$^1A_2$	0.00	0.01	0.00	-0.01	-44.05	-0.03	51.47	0.00	0.09
$^1B_2$	0.03	-0.22	-36.46	-126.13	0.61	0.21	0.53	-0.44	0.05
$^3B_1(0)$	0.00	0.00	0.00	0.00	0.02	52.85	0.00	0.00	0.00
$^3B_2(0)$	0.00	0.00	0.00	-0.02	0.00	0.00	0.00	0.00	48.10
$^3A_2(0)$	0.00	0.00	0.00	-52.85	0.00	0.00	0.00	-48.10	0.00
$^3B_1(+)$	0.00	-0.02	-52.85	0.00	0.00	0.00	0.00	-20.60	0.00
$^3B_2(+)$	0.02	0.00	0.00	0.00	0.00	0.00	20.60	0.00	0.05
$^3A_2(+)$	52.85	0.00	0.00	0.00	0.00	0.00	0.00	-0.05	0.00
$^3B_1(-)$	0.00	0.00	0.00	0.00	20.60	0.00	0.00	0.00	0.00
$^3B_2(-)$	0.00	0.00	-48.10	-20.60	0.00	-0.05	0.00	0.00	0.00
$^3A_2(-)$	0.00	48.10	0.00	0.00	0.05	0.00	0.00	0.00	0.00

S5: Kinetic Modelling and Global Fit

The kinetic model that was used to fit the populations in Figure 4 of the main manuscript can be summarized as $S_2 \rightarrow S_1 \rightarrow S_0$. Its rate law can be written as:

$$\frac{\partial}{\partial t}\begin{pmatrix} S_2(t) \\ S_1(t) \\ S_0(t) \end{pmatrix} = \begin{pmatrix} -k_{21} & 0 & 0 \\ k_{21} & -k_{10} & 0 \\ 0 & k_{10} & 0 \end{pmatrix} \cdot \begin{pmatrix} S_2(t) \\ S_1(t) \\ S_0(t) \end{pmatrix}. \tag{1}$$

Here, k_{21} is the $S_2 \rightarrow S_1$ rate and k_{10} is the $S_1 \rightarrow S_0$ rate.

Integration of this system of differential equations leads to the following expressions for the populations:

$$\begin{pmatrix} S_2(t) \\ S_1(t) \\ S_0(t) \end{pmatrix} = \begin{pmatrix} S_2^0 & 0 & 0 \\ -\frac{k_{21}S_2^0}{k_{21}-k_{10}} & \frac{k_{21}S_2^0+(k_{21}-k_{10})S_1^0}{k_{21}-k_{10}} & 0 \\ \frac{k_{10}S_2^0}{k_{21}-k_{10}} & -\frac{k_{21}S_2^0+(k_{21}-k_{10})S_1^0}{k_{21}-k_{10}} & S_1^0+S_2^0 \end{pmatrix} \cdot \begin{pmatrix} \mathrm{e}^{-k_{21}t} \\ \mathrm{e}^{-k_{10}t} \\ 1 \end{pmatrix}, \tag{2}$$

where S_2^0 is the initial population of S_2 and S_1^0 the one for S_1.

The functions $S_2(t)$, $S_1(t)$, and $S_0(t)$ were then fitted in a global least-squares fashion to the population data from the trajectories of 9H-adenine and 9H-2-aminopurine. Fitting was performed with `gnuplot` 4.6[1] using the Marquardt-Levenberg algorithm. The fitting parameters were the two rate constants k_{21} and k_{10}, which are related to the time constants by $\tau_i = 1/k_i$.

Error estimates for the time constants were calculated using the bootstrapping methodology, which was first applied in the case of surface hopping computations by Truhlar and coworkers.[2] This very general error estimation method is based on random resampling with replacement. For example, for an ensemble of n trajectories, generating one bootstrap resample amounts to randomly drawing n trajectories, where trajectories are allowed to be drawn multiple times. From this resample of n trajectories, one can compute the popula-

tions, and from fitting those one can obtain the two time constants τ_{21} and τ_{10}. This process of generating resamples and fitting them was then repeated 1000 times for the trajectories of 9H-adenine and 9H-2-aminopurine. This lead to a distribution of time constants, from which the errors of the time constants can be computed. The error estimates given in the paper are the standard deviations of these distributions. We note here that these errors only describe the uncertainty in the populations due to the finite number of trajectories; the systematic errors due to the level of theory and the dynamics method are not included.

References

(1) Williams, T.; Kelley, C. gnuplot 4.6. 2014; see http://www.gnuplot.info.

(2) Nangia, S.; Jasper, A. W.; Miller, T. F.; Truhlar, D. G. Army Ants Algorithm for Rare Event Sampling of Delocalized Nonadiabatic Transitions by Trajectory Surface Hopping and the Estimation of Sampling Errors by the Bootstrap Method. *J. Chem. Phys.* **2004**, *120*, 3586–3597.