

Photochemical Ring Opening of Oxirane Modeled by Constrained Density Functional Theory

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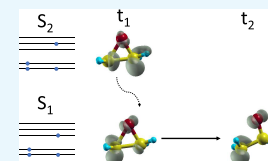


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ABSTRACT: A constrained density functional theory/classical trajectory surface hopping study of the photochemical dissociation of oxirane (CH_2O) is presented. The calculations confirm the Gomer–Noyes mechanism for the initial reaction and agree largely with experimental photolysis data including reaction yields. The calculated yields, however, depend both on temperature and its modeling. The timescales of the various reaction steps are well below 100 fs, similar to previous time-dependent density functional calculations. At variance with those, however, the present calculations obey Kasha's rule, i.e., the photoreaction is initiated in the energetically lowest excited state.



1. INTRODUCTION

Photoinduced nuclear reorganization processes such as photoisomerization and light-stimulated reactions are common in nature, e.g., for photosynthesis, as well as of immense importance for technical applications such as photocatalysis. They may also be destructive, as seen by the photodegradation of many materials. Therefore, it is highly desirable to thoroughly understand photochemical reactions and to be able to model them computationally with predictive accuracy. Photochemical reaction paths access high-energy intermediates and thus allow to overcome large activation barriers in a short period of time. Thereby, the Born–Oppenheimer approximation, i.e., the assumption that the nuclei move on a single potential energy surface (PES) and that the electrons adjust immediately to any change in the nuclear position, may no longer hold, and non-adiabatic effects can become relevant. Moreover, the computational description of excited-state potential energy surfaces is a serious computational challenge.

Many-body perturbation theory provides a systematic and well-founded approach to calculate electronic excitation energies.^{1,2} Here, one solves in the first step the equation of motion for the one-particle propagator using Hedin's GW approximation to self-energy.³ In the second, step the electron–hole pair excitation energies are obtained from the poles of the interacting two-particle Greens' function. A practical scheme of solving for the poles—known as the Bethe–Salpeter equation (BSE) approach⁴—is given by a diagrammatic expansion of the electron–hole propagator in terms of the scattering kernel. This GW-BSE approach allows for the accurate modeling of excited-state PES.^{5,6} However, this method is associated with considerable numerical effort, limiting its application to relatively small systems and short-dynamics time intervals. This holds as well for correlated wave function methods such as multireference configuration interaction (MR-CI)⁷ or the complete active state self-consistent field method.⁸ Time-dependent density functional theory (TD-DFT),⁹ most frequently used within the Tamm–

Dancoff approximation,¹⁰ is a numerically more efficient approach to the calculation of excited-state PES.^{11,12} It works usually well for geometries near their equilibrium, but, within the typically applied approximations, has some limitations as, e.g., the underestimation of charge transfer and Rydberg excitations,¹³ an underestimation of triplet excitation energies,¹⁴ and difficulty to describe high-lying excited states.¹⁵ Constrained density functional theory (cDFT) is another numerically highly efficient and robust scheme to calculate optical excitation energies.^{16–19} Excited-state PES calculated within cDFT were recently successfully used to model the dynamics of optically driven surface phase transitions.^{20,21} In these studies, however, the occupation of the excited states was either frozen throughout the entire phase transition²⁰ or adjusted to match the experimentally measured electronic temperature.²¹ Moreover, the structural reorganization corresponding to the phase transition was limited to geometries close to the equilibrium, and the hopping between different potential energy surfaces (PES) has not been taken into account. A reliable direct assessment of photochemical reactions, however, requires a study of the entire reaction mechanisms including excess energy leading to PES surface hopping. Such a study is reported in the present work, where we model the oxirane ring opening using cDFT in conjunction with Tully's fewest switches surface hopping (FSSH) algorithm²² as implemented in the Libra-X package.²³

Oxirane (ethylene oxide, $(\text{CH}_2)_2\text{O}$), a three-member ring consisting of one oxygen atom and two carbon atoms, has been serving as a model for photochemistry for a long time.^{11,24–28}

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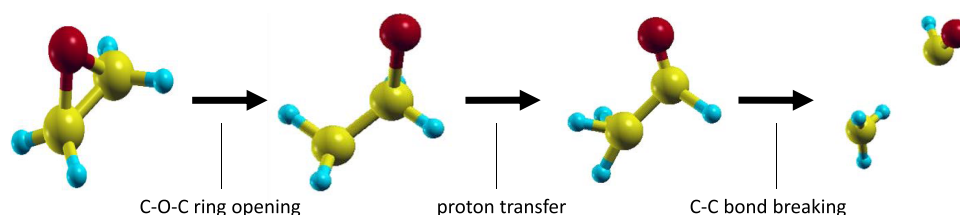


Figure 1. Gomer–Noyes mechanism²⁴ for the photochemical reaction of oxirane. The initial ring opening is followed by proton transfer before the reaction is finalized by C–C bond breaking.

Gomer and Noyes²⁴ found methane, ethane, hydrogen, and carbon monoxide to be the principal products of the photochemical decomposition of oxirane and suggested

$(\text{CH}_2)_2\text{O} + \hbar\omega \rightarrow \text{CH}_3 + \text{HCO}$ ($\text{H} + \text{CO}$) to be the primary process of the reaction, cf. Figure 1. This mechanism was confirmed experimentally by Kawasaki et al.²⁷ Interestingly, in this theoretical work, it was suggested that the photochemical ring opening is facilitated by occupation of the second excited state S_2 , while the first excited state S_1 was found to be a nonreactive channel, which can be energetically tapped, however, by the reactive S_2 state. This seems to contradict Kasha's rule²⁹ that suggests that the first excited state is the most likely candidate for the initiation of photochemical reactions. The present cDFT/FSSH study aims at identifying the most relevant states for the oxirane photochemical reactions and at exploring the influence of the temperature modeling. To that end, we perform non-adiabatic molecular dynamics (NAMD) calculations both within the microcanonical NVE ensemble and within the canonical NVT ensemble.

2. METHODOLOGY

The present calculations are based on spin-polarized density functional theory within the generalized-gradient approximation using the PBE functional³⁰ in the Quantum Espresso³¹ implementation. Norm-conserving Troullier–Martins pseudo-potentials³² are used to describe the electron–ion interaction. The electron states are expanded in a plane-wave basis up to an energy cutoff of 70 Ry. Oxirane is modeled within an $11 \times 11 \times 11 \text{ \AA}^3$ supercell.

Excited-state PES are calculated using cDFT. While the term “cDFT” can be used to describe various constraints like charge, spin, or occupation numbers,¹⁶ we refer to the latter case, i.e., occupying the Kohn–Sham orbitals in a non-Aufbau manner, using occupation constraints.^{17–19,33} A schematic of this cDFT method is shown in Figure 2. This procedure goes by different names, and besides cDFT, it can be also referred to as ΔSCF ,³⁴ ΔDFT ,³⁵ or excited-state DFT.³⁶

Tully's FSSH algorithm²² has been employed to accommodate for non-adiabatic effects. The NAMD calculations were performed using the Libra-X package,²³ which uses the Kohn–Sham orbitals from the cDFT calculations to approximate the wave functions of the excited systems via Slater determinants. The active electronic state of the system determined by FSSH is used for structural relaxation, which means that only one electronic state contributes to the evolution of the NAMD. The non-adiabatic character of the MD is given by the possibility of swapping between PES and by this swapping between the electronic states used to evolve the system. Time steps of 5 as and 0.25 fs have been chosen for the integration of the Schrödinger equation in the FSSH algorithm and the molecular dynamics, respectively. The

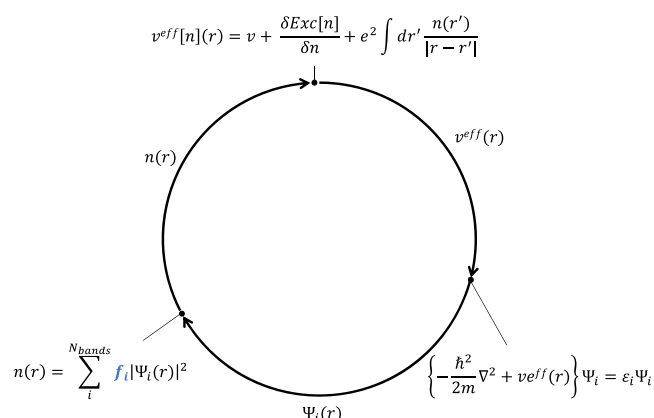


Figure 2. Constraint DFT cycle used for excited-state calculations. In contrast to DFT, cDFT uses the weights f_i , also referred to as occupation numbers, for the calculation of the electronic density $n(r)$. These weights are fixed during the cDFT calculation, and therefore, the Kohn–Sham orbitals can be occupied in a non-Aufbau manner to simulate an excited electronic state.

atomic temperature was controlled in the NVE ensemble by using randomly generated and appropriately scaled initial velocities. Additionally, calculations were performed that model an NVT ensemble with the Nosé–Hoover chain thermostat³⁷ using a chain length of 5 and an effective relaxation time of 24.4 fs. Thereby, the chain length determines the accuracy of the thermostat concerning oscillation in the temperature,³⁷ and the effective relaxation time determines the coupling strength to the heat bath.³⁷ Usually, the frequency corresponding to the effective relaxation time should have the same order of magnitude as characteristic frequencies of the nuclear degrees of freedom.²³ With most of the characteristic frequencies of oxirane being between 1000 and 3000 cm^{-1} ¹³⁸ and the frequency corresponding to the effective relaxation time being 1367 cm^{-1} , this criteria is fulfilled. The NAMD calculations consider, in addition to the electronic ground state (S_0), the first three single electron excited states (HOMO $\rightarrow$ LUMO (S_1), HOMO $\rightarrow$ LUMO+1 (S_2), and HOMO $\rightarrow$ LUMO+2 (S_3)). While the character of the excited states changes during the evolution of the system (as seen for example in Figure 9), the terms S_0 for the ground state, S_1 for the first excited state, etc. will still be used for the sake of clarity. The excited states are modeled with cDFT assuming no spin flips. Smearing of the occupation numbers based on the Fermi distribution function was employed in order to mimic a multiconfigurational behavior in the case of (quasi-)degeneracy of states.²³ Thereby, a broadening parameter of 0.01 Ry is used, and the smearing is updated after 30 electronic iterations. We restrict our simulations to reactions initiated in the second excited state (S_2) and from slightly randomized $\text{C}_2\text{H}_4\text{O}$ ground-state geometries, i.e., each ion displaced by max. 0.05

Å in each direction. A number of 50 trajectories are calculated and averaged to model photoreactions taking place at temperatures of 30, 77, 100, 150, 300, and 400 K.

The time evolution of the photoreaction is monitored by evaluating the occupation numbers of the electronic states, the charge distribution, and the molecular geometries. With respect to the latter, we use thresholds listed in the [Supporting Information](#) in order to classify the reaction products. In the case of state crossing, which includes the active state, which can either happen permanently (which, however, was not observed) or temporarily due to the smearing, the indexing of the states swaps with the states. If, for example, the active state S_v crosses S_0 , due to indexing changes, then S_1 becomes S_0 and vice versa. The character of the active state is, however, preserved by the FSSH algorithm as the probability of a hop to the new S_0 state is large since it has the character of the old S_1 state. Since no permanent state crossing is observed, in the analysis, the swaps of the indices are undone by comparing the PES to avoid confusion. Therefore, in this example, the active state would be S_1 before and after the crossing.

3. RESULTS AND DISCUSSION

In [Figure 3](#), the calculated oxirane electron densities corresponding to specific orbitals relevant for the lowest

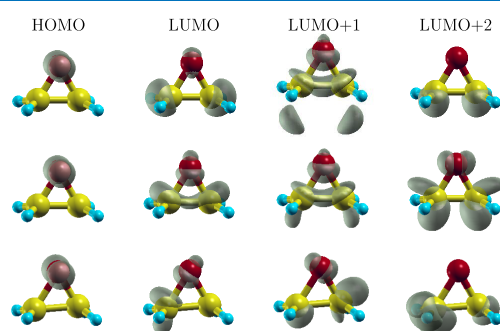


Figure 3. Calculated electron densities corresponding to the orbitals for the states most relevant for the photoreaction of oxirane. The top row shows the densities for HOMO, LUMO, LUMO+1, and LUMO+2 in the structural and electronic ground state. The middle row shows the respective densities corresponding to the orbitals with one electron removed or added, calculated within cDFT, i.e., the highest occupied orbitals for S_0 , S_1 , S_2 , and S_3 . The bottom row shows the same densities for a slightly disturbed geometry with a maximum deviation of 0.05 Å from the ground state.

optically excited states are shown. The ground-state orbital character of states obtained here for HOMO, LUMO, LUMO+1, and LUMO+2 confirm previous DFT-PBE calculations.¹¹ The character of these states is roughly conserved in the S_0 and S_2 excitations, while we observe some mixing of the LUMO and LUMO+1 states upon S_1 excitation. The S_3 excitation calculated here resembles S_2 calculated in [ref 28](#). Moreover, we observe that the excited states depend sensitively on the molecular geometry. This can be seen in the lower part of [Figure 3](#), where the lowest excitations for slightly deformed molecules are shown.

[Table 1](#) shows the cDFT excitation energies of the states S_1 , S_2 , and S_3 and compares them with the singlet excitation energies calculated by other methods as well as with experimental data. It can be seen that the cDFT excitation energies slightly underestimate the measured excitation energies.

Table 1. Oxirane Singlet Excitation Energies (in eV) for cDFT in Comparison with Other Computational Methods as well as with Experimental Data

cDFT	exp.	TDHF ³⁹	TDLDA ³⁹	TDB3LYP ³⁹
6.69	7.24 ^{40–42}	9.14	6.01	6.69
6.76	7.45 ⁴¹	9.26	6.73	7.14
7.26	7.88, ⁴⁰ 7.89 ⁴¹	9.36	6.78	7.36
		9.56	7.61	7.85
		9.90	7.78	8.37
		9.93	8.13	8.39
		8.15	8.40	

In the following, we present NVE calculations initiated in the second excited state S_2 , resulting from an electron transfer HOMO→LUMO+1. As seen from [Figure 4](#), within a few femtoseconds, the excitation is mostly transferred to S_1 and in some cases to S_3 before it is quenched in S_0 . However, even after 250 fs, there is still a sizable number of molecules in an electronically excited configuration.

As can be seen from [Figure 5](#), where the formation probabilities of the reaction products are plotted vs. time for different temperatures, the Gomer–Noyes mechanism is the most dominant process in the NAMD simulations, in agreement with measured data.²⁷ After 30–40 fs, the ring opening (CH_2COH_2 formation) is completed in the majority of the excited oxirane molecules. The third reaction step according to Gomer and Noyes, the CH_3COH formation, is essentially completed for most molecules after about 80 fs. The following dissociation of the molecule into $\text{CH}_3 + \text{COH}$ can also be observed in some cases but not in the quantity observed experimentally. This is the same finding as in the previous work of [ref 11](#). The processes above compete with oxygen and hydrogen abstraction. The influence of the initial temperature on the occupation numbers of the respective states and on the reaction kinetics is limited. The latter can be seen from the nearly constant position of the peak maxima in [Figure 5](#). The calculated reaction times for the $\text{C}_2\text{H}_4\text{O} \rightarrow \text{CH}_2\text{COH}_2$ reaction with 18–45 fs and for the $\text{CH}_2\text{COH}_2 \rightarrow \text{CH}_3\text{COH}$ with 43–85 fs match largely the results of [ref 11](#) (20–40 and ~70 fs).

The situation changes when the calculations are performed in the NVT ensemble using the Nosé–Hoover thermostat. This is shown in [Figure 6](#) for the occupation numbers. Both calculations modeling a temperature of 100 and 300 K show a rapid quenching of the electronic excitation. Already after 80 fs, the majority of molecules has returned to the electronic ground state S_0 . Apart from the ground state, S_1 is then the only other relevant excitation. This contrasts with the NVE calculations, where additionally S_2 and S_3 excited molecules occur throughout the simulation time.

The different excitation scenarios observed in the NVE and NVT ensembles lead also to different reactions as shown in [Figure 7](#). The energy dissipation due to the thermostat causes a slowing of the reactions, which inhibits C–C bond breaking and may even lead to a reversal of the first Gomer–Noyes reaction step



after about 70 fs. Additionally, we find the temperature itself to have a much more pronounced influence on the NVT calculation than that observed for NVE. Higher temperatures,

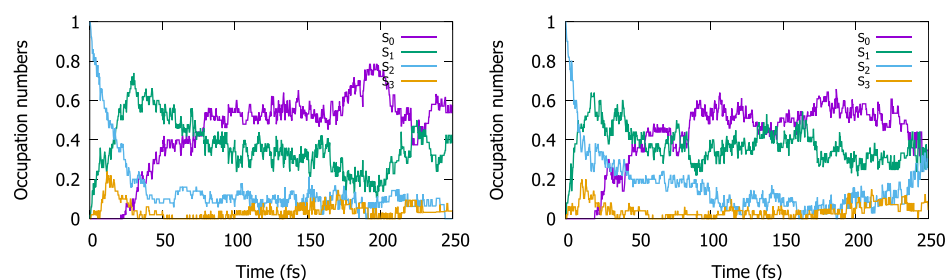


Figure 4. State populations (averaged over up to 50 trajectories) vs. time for NVE calculations modeling an initial temperature of 100 K (left) and 300 K (right).

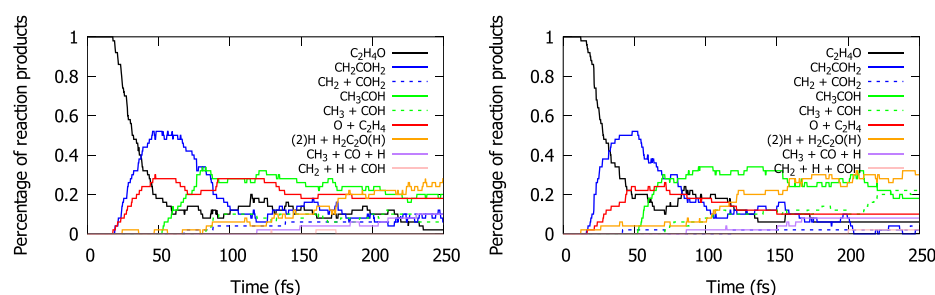


Figure 5. Reaction products vs. time in the microcanonical NVE ensemble for temperatures of 100 K (left) and 300 K (right). With the peaks at nearly the same time, we see little influence of the temperature on the reaction times.

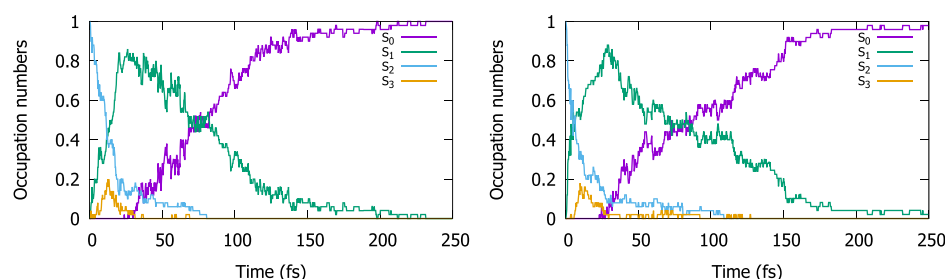


Figure 6. State populations (averaged over 50 trajectories) vs. time for NVT calculations modeling a temperature of 100 K (left) and 300 K (right).

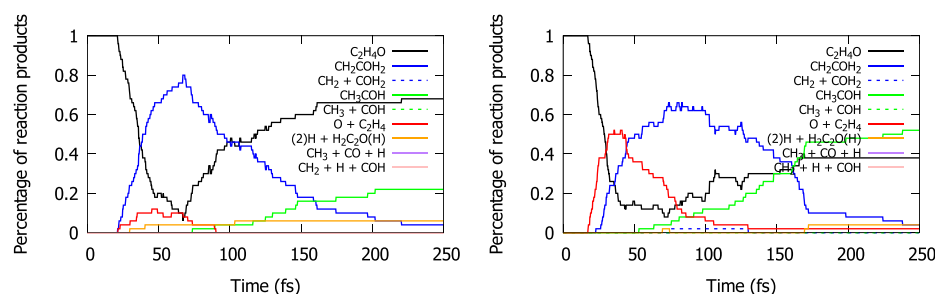


Figure 7. Reaction products vs. time in the canonical NVT ensemble for temperatures of 100 K (left) and 300 K (right).

for example, considerably prolong the time period where CH_2COH_2 molecules constitute the majority of species.

Figure 8 summarizes the influence of the temperature on the relative yield of the reaction products available after 250 fs. As expected, the influence of the temperature is much more pronounced in the case of NVT calculations than that observed for the NVE ensemble. In the latter case, there occur slightly less O abstractions and some more H abstractions at higher temperature. In the case of the O abstractions, this is due to a faster loss of symmetry of the molecule. As shown by ref 11 and verified in this work (see below), the O abstraction occurs if the O and C ions form an isosceles triangle. With a higher

initial velocity, this symmetry is broken faster, reducing the probability of O abstractions. In the case of the H abstractions, an increase with temperature is observed since the C–H bond can break with a higher kinetic energy. The slowing of the reactions as modeled by the NVT ensembles also influences the end products as seen in Figure 8 (right). Ion abstraction is hindered in NVT ensembles, lowering the amount of $O + C_2H_4$ and $(2)H + H_2C_2O(H)$ products at every temperature. A clear dependence on the temperature can be seen for the C_2H_4O and $CH_3 + COH$ products, which prevail at low and high temperatures, respectively.

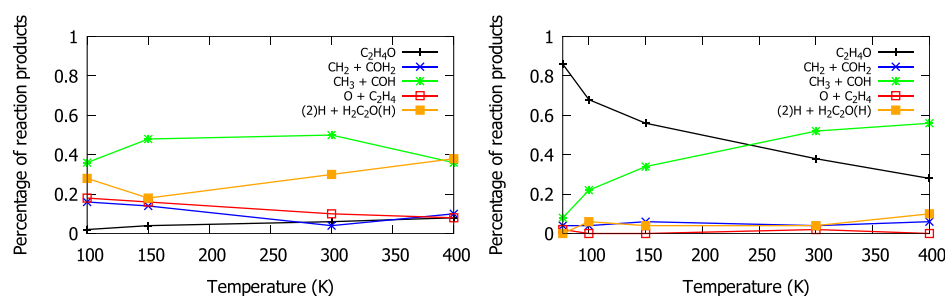


Figure 8. Percentage of reaction products vs. temperature after 250 fs integration time calculated in the microcanonical *NVE* (left) and canonical *NVT* ensembles (right). In the interest of clarity of presentation, reactions with and without C–C bond breaking are not discriminated.

Table 2. Calculated Reaction Yields after 250 fs Simulation Time in Comparison to Measured Data after Excitation with 174–147 nm Light^{27a}

temperature (K)	<i>NVE</i>				<i>NVT</i>					exp.
	100	150	300	400	77	100	150	300	400	
CH ₃ +COH	1	1	1	1	1	1	1	1	1	1
CH ₂ +COH ₂	0.42	0.29	0.08	0.28	0.50	0.18	0.17	0.08	0.11	0.00–0.17
O+C ₂ H ₄	0.50	0.33	0.20	0.22	0.25	0.00	0.00	0.04	0.00	0.10–0.58
(2)H+H ₂ C ₂ O(H)	0.78	0.38	0.60	1.06	0.00	0.27	0.12	0.08	0.18	0.08

^aAll yields are normalized to the CH₃+COH formation. Reactions with and without C–C bond breaking are not discriminated.

A quantitative comparison with the experimental data²⁷ measured at 77 K is presented in Table 2. Both *NVE* and *NVT* calculations overestimate the probability of CH₂+COH₂ formation at low temperature, while the room temperature data are closer to the experimental findings. In the case of the oxygen abstraction, the *NVE* calculations seem to predict a realistic probability, while *NVT* ensembles in some cases do not show any O abstraction, in contrast to experiment. In the case of hydrogen abstraction, all *NVE* calculations overestimate the measured yield, while the low-temperature *NVT* calculations do not find any H abstraction. This is consistent with the expectation that the complete neglect of energy dissipation in *NVE* calculations leads to an overestimation of kinetic excess energy, while due to the unrealistically fast energy dissipation to the *NVT* thermostat, there is not enough energy available for bond breaking. The fact that *NVE* ensembles provide a more realistic description of the O abstraction compared to the H abstraction may be related to the fact that the former reaction occurs soon after the excitation when energy dissipation effects are not yet important. Altogether, the present findings suggest that neither *NVE* nor *NVT* calculations are ideally suited to describe the energy dissipation on the timescales investigated here. Possibly, the microscopic description of the energy dissipation by means of larger atomistic ensembles, unfortunately beyond our computational limitations, could resolve these issues.

Finally, based on the averaged occupation numbers and the electronic densities, we address the question of which states drive the photochemical reactions of oxirane. The ring opening, the first step in the Gomer–Noyes mechanism, is found to be correlated to the occupation of the S₁ state. This can clearly be seen in Figures 4, 5, 6, and 7. Moreover, as demonstrated in the Supporting Information by means of curve fits, there is even a quantitative correlation between S₁ occupation and the ring opening. The electronic density corresponding to S₁ during the reaction can be seen in Figure 9. The present calculations thus, in deviation from the findings in ref 11, indicate the validity of Kasha's rule for the Gomer–

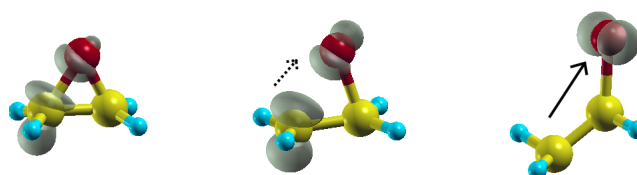


Figure 9. Calculated electronic density corresponding to the excited orbital of the first excited state (S₁) during the ring opening reaction path after 5, 15, and 30 fs integration time.

Noyes reaction: While Tapavicza et al. found that the reaction is triggered by the excitation of the S₂ state, which switches later on in the reaction to the S₁ state via orbital crossing, we do not observe such an orbital crossing. The reaction starts after an actual hop from the S₂ to the S₁ state. We attribute this deviation to the sensitivity of the oxirane excited states to changes in the occupation numbers and structural distortions as discussed above, cf. Figure 3.

In the case of the O abstraction, both the occupations of the S₁ and the S₂ state are found to trigger the reaction. In most of the cases, both states participate in the reaction, first, the S₂ state and then the S₁ state, though both states can individually cause the reaction. The reaction requires that the molecule is nearly symmetric, i.e., in its relaxed ground state. With no preference to each side, both states pushes the O ion away from the rest of the molecule. This finding is in accordance with ref 11. Electronic densities during this reaction can be seen in Figure 10.

The proton transfer (second step in the Gomer–Noyes mechanism) and the following C–C bond breaking (last step in the mechanism) occur in the S₀ ground state, which is again in accordance with the findings in ref 11. Additionally, we found that while this reaction happens due to excess kinetic energy, the reaction can be stopped by occupation of the S₁ state, which prohibits the proton transfer. The electronic densities during this inhibited reaction can be seen in Figure 11. The PES surface hopping necessary for this process occurs naturally via the FSSH algorithm, in contrast to ref 11. The

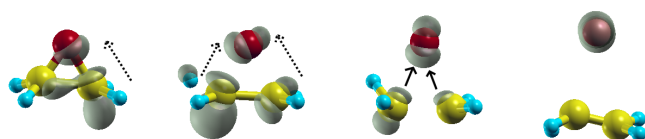


Figure 10. Electronic densities during the O abstraction reaction. The oxirane molecule is shown at 0, 10, 20, and 35 fs. The first two images show the density of the highest occupied orbital of the excited S_2 state; the latter two densities reflect the highest orbital of the S_1 state.

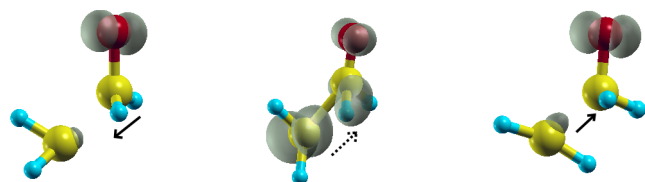


Figure 11. Electronic densities corresponding to the excited orbitals of the respective electronic states during an inhibited H transfer. The H transfer is initiated by the S_0 state (left, at 135 fs). Further 10 fs later, the H ion is repelled by the S_1 state (middle, at 145 fs), and finally, the molecule returns to S_0 (right, at 155 fs).

identifications of the states responsible for the reactions via electronic densities are supported by means of the averaged occupation numbers, which can be found in the [Supporting Information](#).

4. CONCLUSIONS

The photoreaction of oxirane has been modeled with constrained DFT in conjunction with Tully's FSSH algorithm. The present results confirm the Gomer–Noyes mechanism, i.e., a ring opening followed by an internal proton transfer concluding with a C–C bond breaking. After about 30–40 fs, the ring opening is completed. This part of the reaction is driven by the lowest excited state S_1 , in accordance with Kasha's rule. Further molecular decompositions take place in the ground state S_0 by means of excess kinetic energy on a similar timescale. If the molecule is nearly symmetric, then an oxygen abstraction can occur, which is driven by the S_2 or S_1 state. The computationally predicted reaction yields are in qualitative agreement with measured data. Remaining discrepancies are partially due to the description of the energy dissipation. On the one hand, after several hundred femtoseconds NVE ensembles are characterized by excess energy, which leads, e.g., to an overestimation of hydrogen abstraction reactions. NVT ensembles based on a Nosé–Hoover thermostat, on the other hand, experience too high cooling rates, which lead to an underestimation of dissociative reactions. Our calculations thus suggest that (i) occupation constrained DFT is a viable alternative to computationally more expensive schemes to describe photoreactions and (ii) underline the importance of a realistic modeling of the energy dissipation in the sub picosecond range, ideally by ensemble calculations, which contain a reasonable, statistically relevant number of molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c03483>.

Numerical parameters for structure classification, the identification of the responsible occupied excited states

for the reactions via occupation numbers, and a short discussion about conical intersections of the S_1 and S_0 state (ZIP)

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Notes

The authors declare no competing financial interest.

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Photochemical Ring Opening of Oxirane Modeled by Constrained Density Functional Theory

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Classification of reaction products:

Table S1: Parameter thresholds used for the classification of the reaction products.

reaction prod.	max. O-C-C angle	max. # H ions at C	C-C dist.	min. C-H dist.	min C-O dist.
C ₂ H ₄ O	<100°	2	-	<1.8 Å	<2.0 Å
CH ₂ COH ₂	>100°	2	<2.6 Å	<1.8 Å	<2.0 Å
CH ₂ + COH ₂	-	2	>2.6 Å	<1.8 Å	<2.0 Å
CH ₃ COH	-	3	<2.6 Å	<1.8 Å	<2.0 Å
CH ₃ + COH	-	3	>2.6 Å	<1.8 Å	<2.0 Å
O + C ₂ H ₄	-	-	-	-	>2.0 Å
(2)H + H ₂ C ₂ O(H)	-	-	<2.6 Å	>1.8 Å	<2.0 Å
CH ₃ + CO + H	-	3	>2.6 Å	>1.8 Å ^a	<2.0 Å
CH ₂ + H + COH	-	3	>2.6 Å	>1.8 Å ^b	<2.0 Å

The distance^{a,b} refer to the proton in the COH and CH₃ cluster, respectively

Identification of the occupied electronic states for specific reactions via the occupation numbers:

The ring opening is found to be correlated to the occupation of the S₁ state. As seen in Figs. 4, 5, 6, and 7 in the main text, the ring opening is the most prominent reaction to occur after the occupation of the S₁ state. This can also be seen in Fig. S1 here, where both the percentage of CH₂COH₂ products and the averaged occupation number of the S₁ state are

plotted for the temperatures 100 K, 150 K, 300 K and 400 K (all without thermostat). The data are fitted to an exponential function ($B \left(1 - e^{-\frac{x-a}{t}}\right)$, with x the time), the parameters of the fitted functions are listed in table S2. The striking coinciding of the parameters w and t which show the decay behavior of the curves demonstrate the correlation of the ring opening to the occupation of the S_1 state.

Table S2: Fit parameters of the exponential fits

Temperature	S_1 plotrange	C	d	w	COH_2CH_2 plotrange	B	a	t
400K	[0:30]	0.53	-0.77	8.37	[17.25:57]	0.42	17.88	12.42
300K	[0:20]	0.7	0.14	9.8	[16:50]	0.55	17.1	10.78
150K	[0:29.5]	0.77	0.13	13.15	[18.75:58]	0.53	19.0	12.17
100K	[5.75:43.5]	0.71	1.1	15.56	[19.25:63.5]	0.56	20.0	14.49

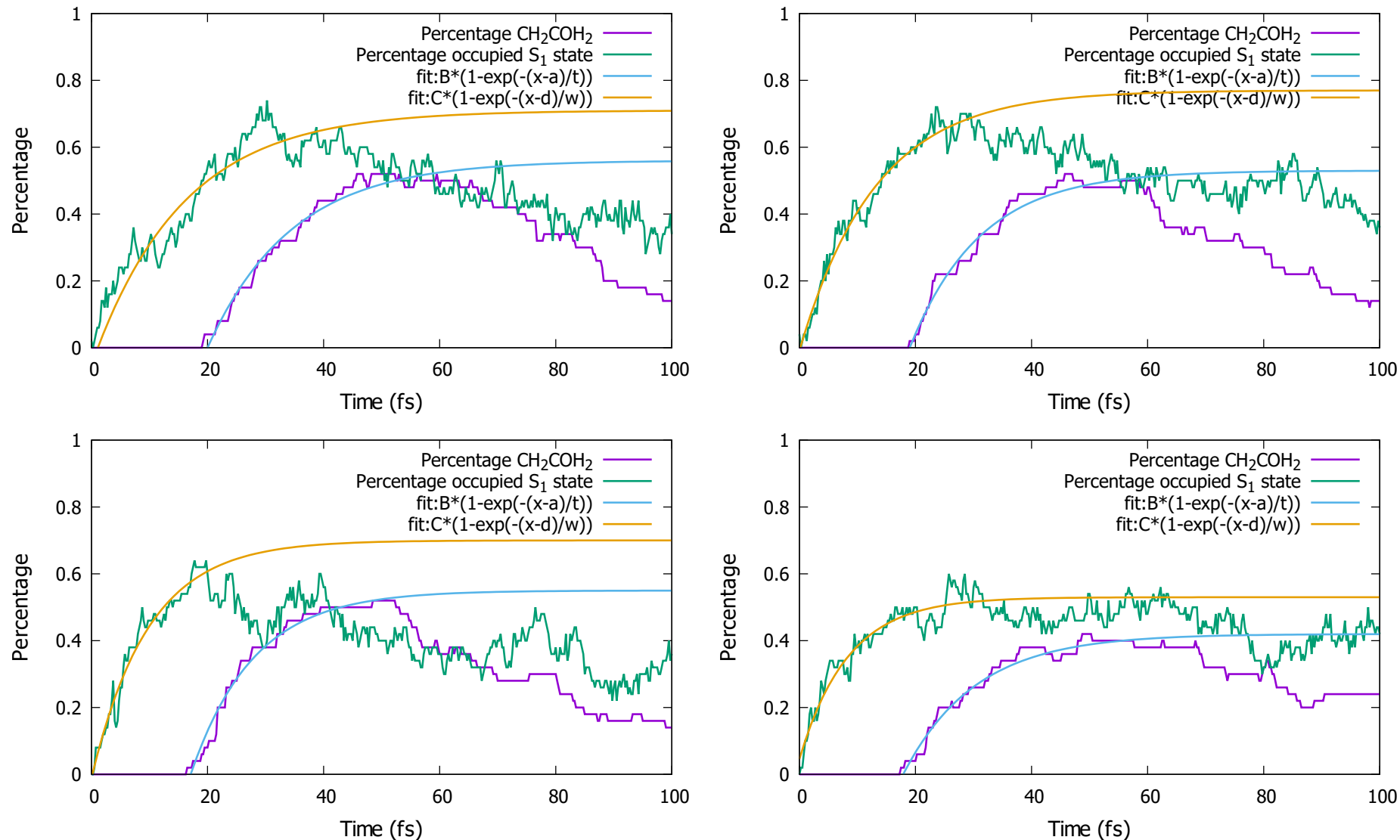


Figure S1: Percentage of the CH_2COH products and of the averaged occupation numbers of the S_1 state for the temperatures 100, 150, 300 and 400 K (left to right and top to bottom), all calculated without thermostat. Both curves are fitted to an exponential function. The similarity of the curves show the correlation between the S_1 state and the ring opening reaction.

The O abstraction is found to happen either in the S_1 or S_2 state in a highly symmetric orientation of the molecule (relaxed groundstate). A higher occurrence of this reaction can be seen if the trajectories starts closer to this configuration, as seen in figure S2.

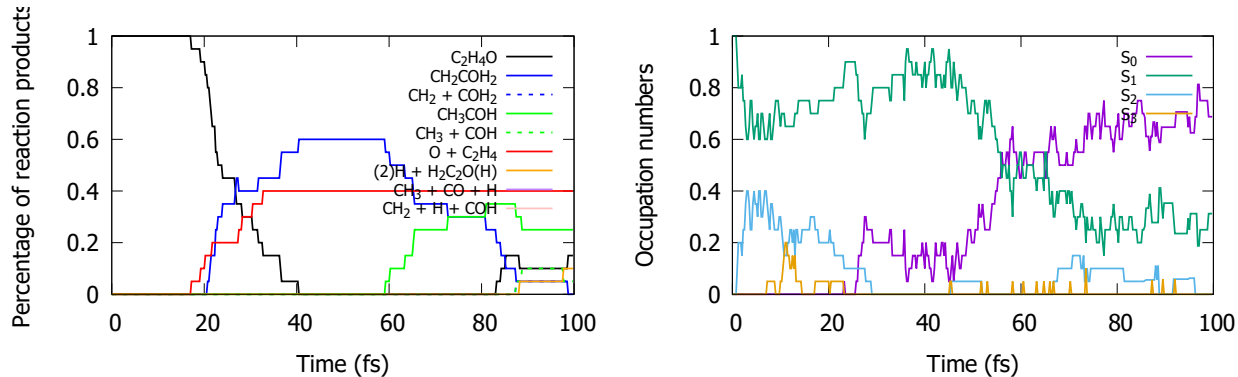


Figure S2: Averaged occupation numbers (right) and percentage of reaction products vs. time. The trajectories starts with a maximum deviation of 0.0025 Å from the symmetric relaxed configuration and with the S_1 state occupied. A temperature of 300 K is simulated via the Nosé-Hoover chain thermostat. In comparison with Fig. 5 and 7 in the main text a higher percentage of O abstraction is seen despite the usage of the thermostat.

The proton transfer is found to happen in the S_0 state. This is supported by the earlier switch to the S_0 state in the trajectories where a proton transfer occurs in comparison to the entirety of trajectories (seen in Figs. S3 to S4).

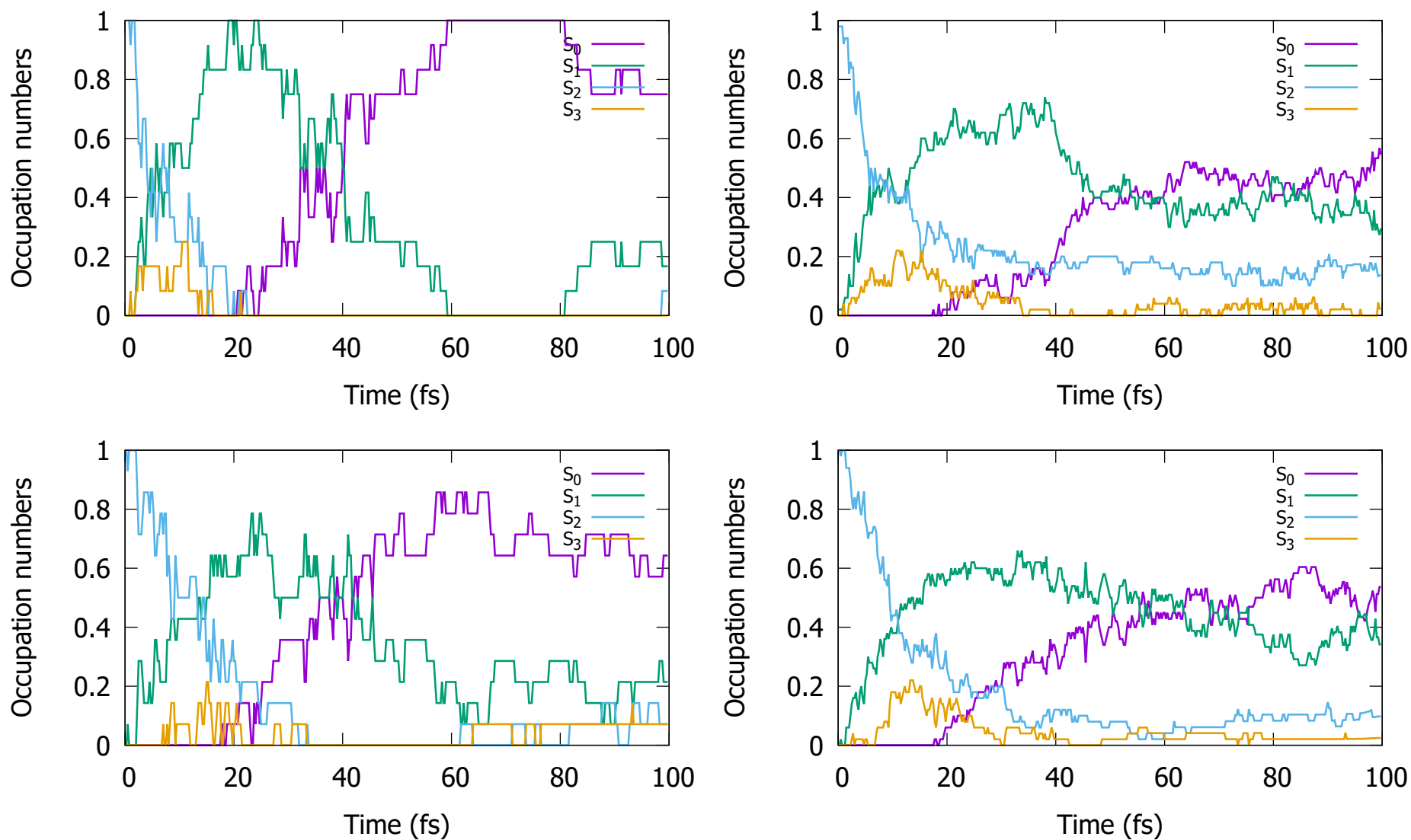


Figure S3: Averaged occupation numbers of the trajectories where a proton transfer occurs (left) and the entirety of trajectories (right) plotted vs. the time. On the top the trajectories for 30 K are plotted, on the bottom the trajectories for 77 K (both without thermostat).

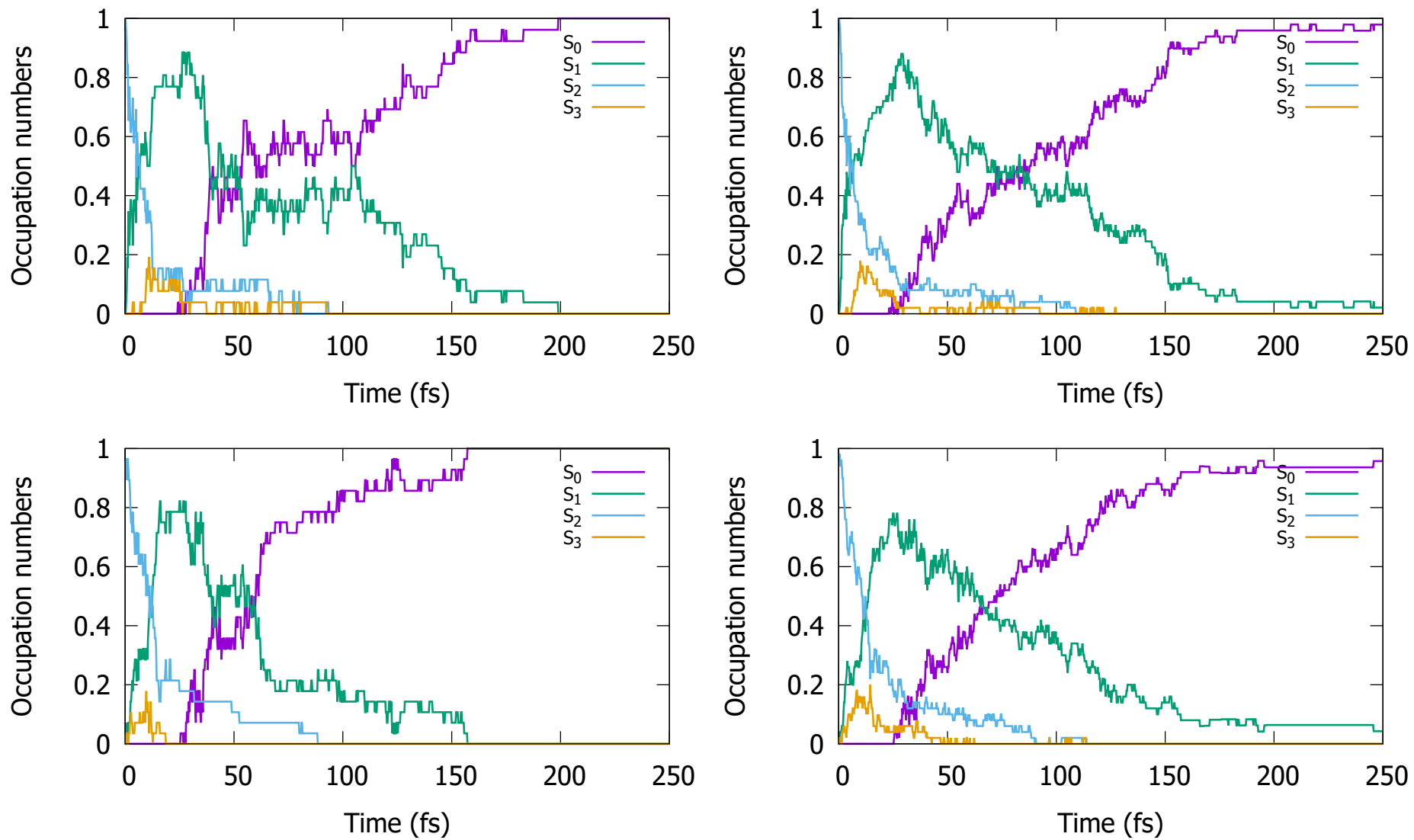


Figure S4: Graphs like in figure S3, but for 300 K (top) and 400 K (bottom), both with usage of the Nosé-Hoover chain thermostat.

Intersections of the S_1 and S_0 state

Tapavicza *et. al.* and Xin *et. al.* report conical intersections of the S_1 and S_0 state during the ring opening reaction.^{1,2} According to Xin *et al.* full degeneracy of the S_1/S_0 states happens at a C-C-O angle of 114° and a C-O bond length of $1.328 \text{ \AA}$.² In our calculations we also observe degeneration of S_0 and S_1 , which starts at C-C-O angle around 111° , if there is little change in the C-O bond length (bond length of $1.5 \pm 0.2 \text{ \AA}$). This corresponds well to the "CI-asym" structure in Ref. 2. The degeneration breaks down due to changes in the C-O bond length or the C-C-O angle becoming too big. This is illustrated in figure S5 and S6. These quantities influence each other and are influenced by the H ions, which is why in figure S5 the degeneracy is lifted at 35 fs but still nearly exists at 45 fs in figure S6 (this structure corresponds roughly to the "CI-asym-tw" structure in Ref. 2), despite the similar angles. During the degeneracy of the states the MD is mostly driven by the remaining velocity of the ions, as both S_0 and S_1 do not provide additional forces as shown by means of their electronic density in figures S9 and S8. The intersection of the S_1 and S_0 PES does not happen however for each trajectory. Due to thermal effects (in both NVE and NVT ensemble, but more frequently in NVT) the degeneracy can be avoided, which happens mostly due to changes in the C-O bond length as illustrated in figure S7. The possibility of degeneracy of the S_1 and S_0 state during the trajectories however does not seem to affect the hopping between the states, the hopping from S_1 to S_0 is likely to happen in both cases as illustrated exemplarily in figures S5, S6 and S7. The hopping probability between S_1 and S_0 seems to be of the same magnitude as hopping from S_2 to S_1 (as it can be seen in figure 4 and 6 in the main text), contrary to the findings of Tapavicza *et. al.*¹

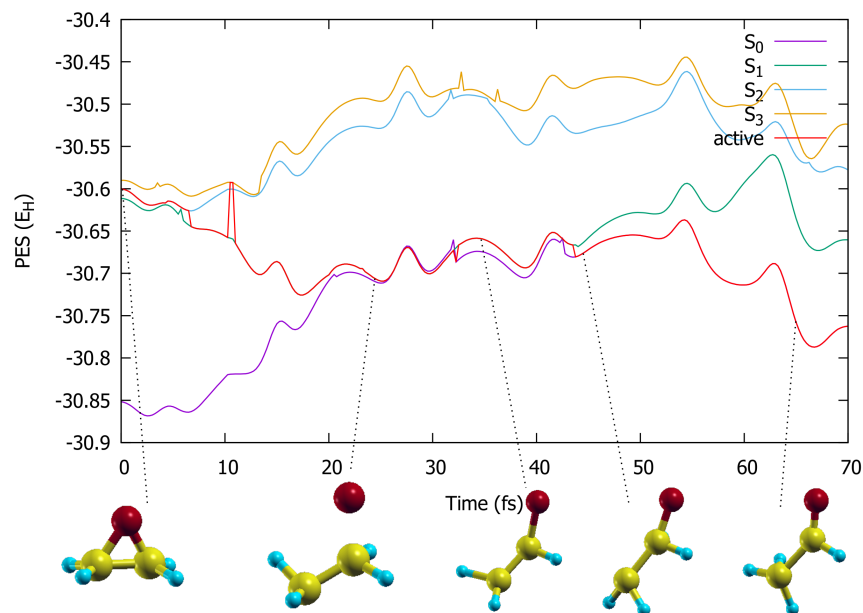


Figure S5: Potential energy surfaces (PES) of a trajectory from a NVE ensemble at 300 K. Beside the PES the current active state of the MD is shown. At 25 fs with a C-C-O opening angle of 111° the S_1 and S_0 state start to degenerate. The degeneracy is later on lifted due to further opening of the C-C-O ring. The rather abrupt drop in energy of the S_0 state at 32 fs is a result of the high number of scf-cycles after which the occupation smearing is updated. A lower number would smooth this out, but would also require more in- and output operations for the Libra-X program, which are chokepoints in the calculations.

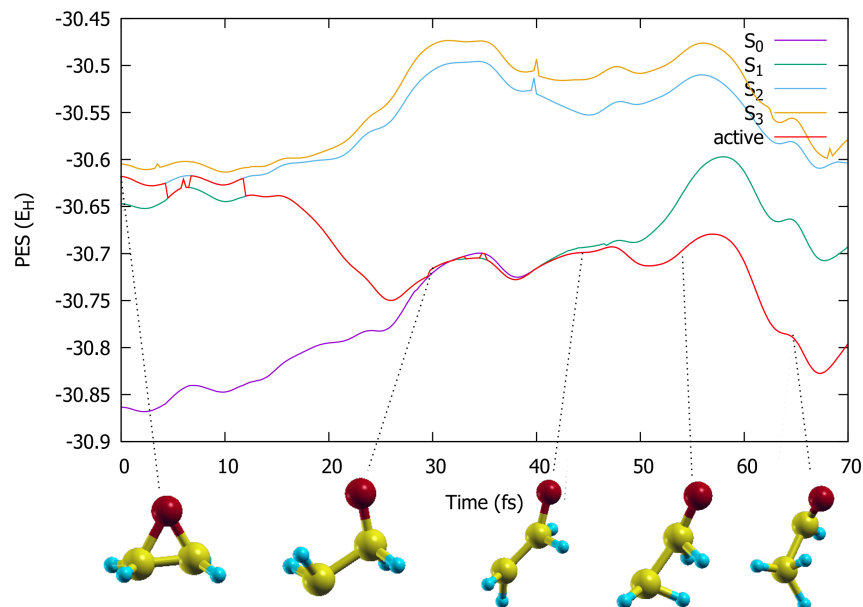


Figure S6: PES like in figure S5 from a NVE ensemble at 150 K. The degeneracy begins at 30 fs at an C-C-O angle of 113° and is broken later on due to further opening and movement of H-ions.

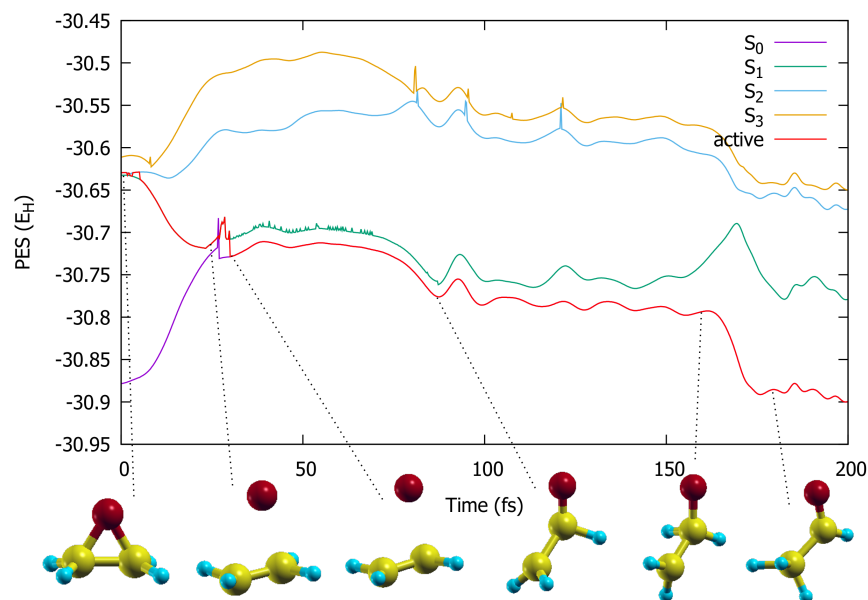


Figure S7: PES like in figure S5 from a NVT ensemble at 150 K. In this case the degeneracy is avoided because of a stretching of the C-O bond (around 30 fs) due to thermal effects. Later on at 90 and 160 fs the degeneracy is also avoided, probably also due to changes in bond length.

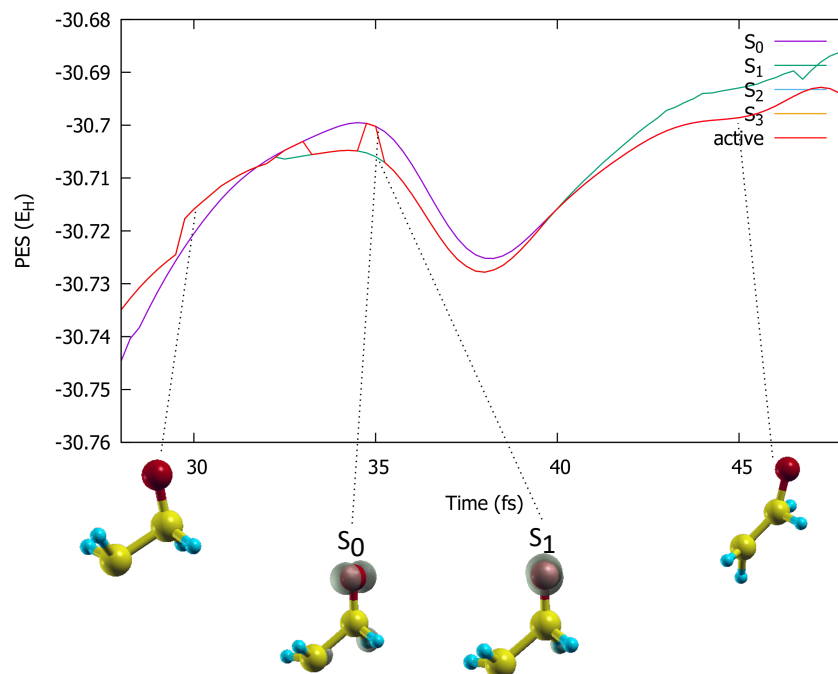


Figure S8: Extract from figure S6 during the degeneracy. A temporary crossing of the S_1 and S_0 state is shown. The character of the states at 35 fs is similar and only differentiated by a rotation of the electronic densities corresponding to the orbitals occupied by the cDFT method. It is to note, that the reordering of the indices for the active state is not in effect: If the active state is shown as S_1 after the crossing, S_0 is the actual active state, as it is energetically higher than S_1 . This means the shown hopping from S_1 to S_0 in the beginning is due to the mentioned preserving of the character of the state due to the FSSH algorithm, as the actual active state is S_1 . After a few "real" hops, the S_0 state resides as the active state.

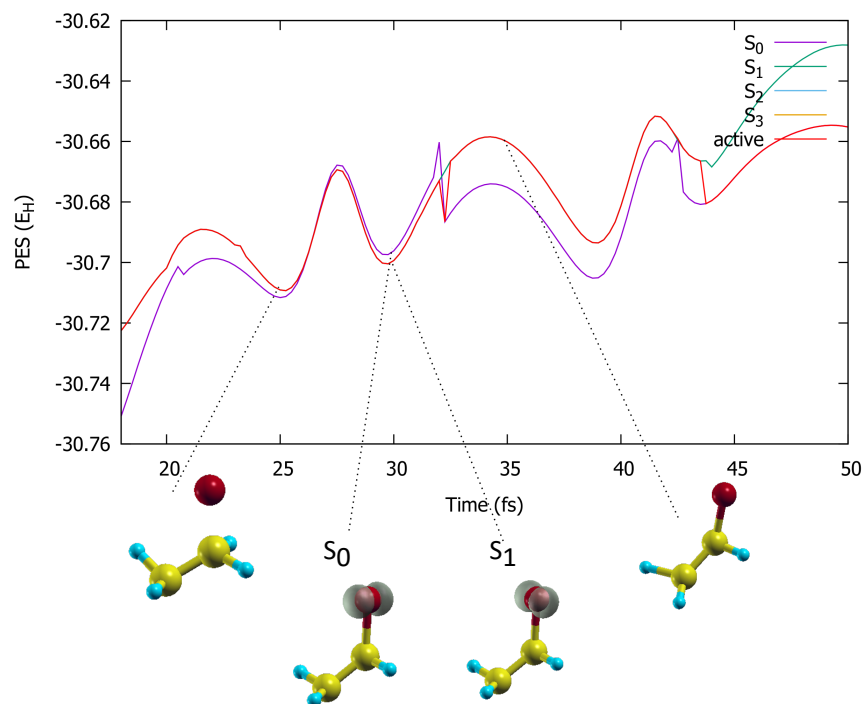


Figure S9: PES like in figure S6 for the NVE trajectory at 300 K. In this case the conservation of the character of the S_1 state does not occur, therefore a "real" hop is happening. At 30 fs the character of the states is again only differentiated by a rotation of the electronic density.

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