Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for: Stable Excited Dication: Trapping on the S$_1$ State of Formaldehyde Dication After Strong Field Ionization

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1 Optimized geometries

The optimized geometries of both neutral and dication formaldehyde are being used in this work. The geometries are shown in Figure S1.

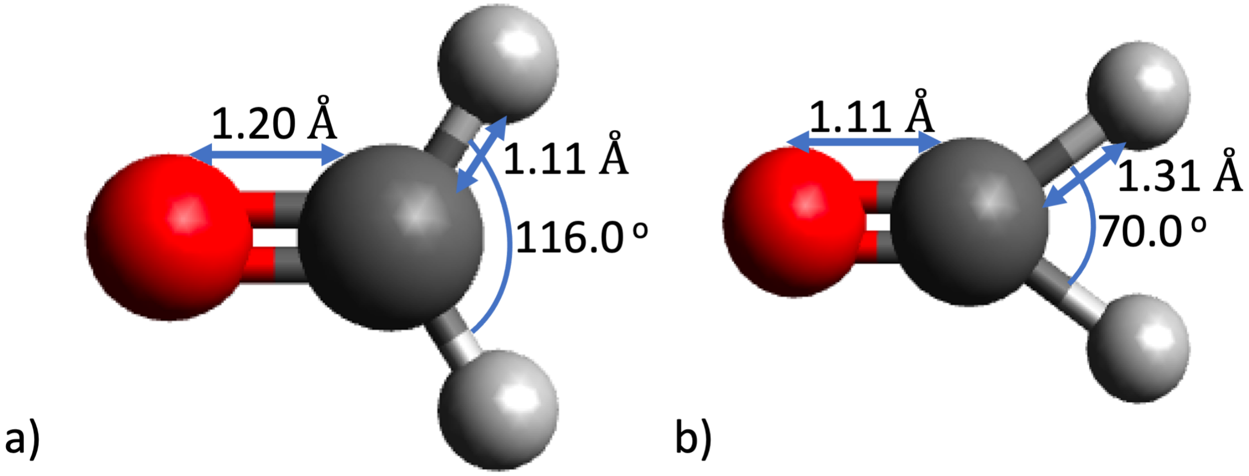

Figure S1: Optimized geometries of a) neutral formaldehyde and b) Dication formaldehyde. The optimizations were done at B3LYP/cc-pVTZ level of theory using Gaussian09.

2 Energies at different levels of theories

Different electronic structure methods are used to calculate the excited states of the dication, and the results are shown in Tables S1 and S2. EOM-EE-CCSD/cc-pVQZ is the most sophisticated method used. The agreement between the methods is very good for the states up to S_3 with the energies varying by up to 0.2 eV. The errors for the higher states are larger with variations of 1 eV or more. Since we are primarily interested in S_1 the results below show that the CASSCF approach used for the dynamics is reliable.

Table S1: Excited state energies of the dication at the neutral geometry of formaldehyde calculated at different levels of theories. All the energies are with respect to the ground state minimum of the dication at the particular level of theory.

Singlets	S_0	S_1	S_2	S_3	S_4	S_5
EOM-EE-CCSD/cc-pVTZ	0.973	4.703	6.550	7.958	10.829	11.632
EOM-EE-CCSD/cc-pVQZ	1.029	4.741	6.601	8.005	10.898	11.69
5SA-CAS(10,10)/cc-pVDZ	0.902	4.822	6.683	8.289	9.850	
10SA-CAS(8,9)/cc-pVDZ	0.926	4.652	6.810	8.074	9.898	10.062
6SA-CAS(8,9)/cc-pVDZ	0.855	4.648	6.825	8.17	9.953	10.128

Table S2: Excited state energies at the minimum of the formaldehyde dication calculated at different levels of theories. All the energies are with respect to the ground state minimum of the dication at the particular level of theory.

Singlets	S_0	S_1	S_2	S_3	S_4	S_5
EOM-EE-CCSD/cc-pVTZ	0	6.064	7.570	8.097	10.467	11.254
EOM-EE-CCSD/cc-pVQZ	0	6.068	7.59	8.086	10.414	11.240
5SA-CAS(10,10)/cc-pVDZ	0	6.004	7.649	8.045	11.336	
10SA-CAS(8,9)/cc-pVDZ	0	5.981	8.055	8.083	11.174	12.08
6SA-CAS(8,9)/cc-pVDZ	0	5.908	7.916	8.014	11.05	11.927

3 Calculation of energetic barrier for the dissociation of CH_2O^{2+} along asymmetric CH stretch on S_1 state.

In order to obtain a better estimate of the barrier along the S_1 surface to break a single CH bond a constrained optimization was performed, as shown in Figure S2.

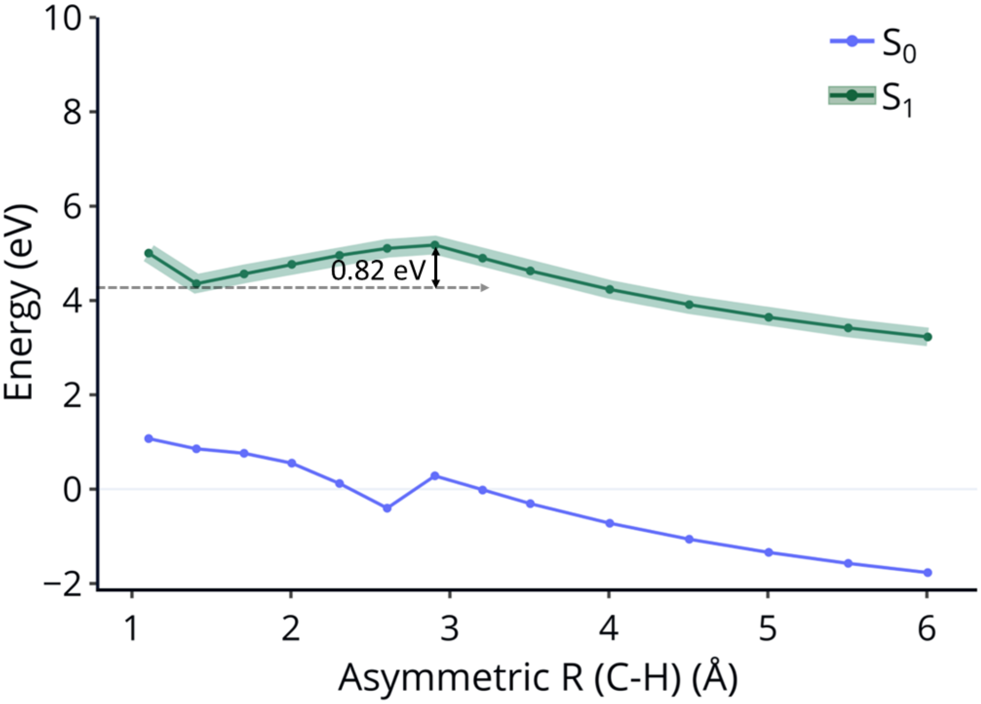

Figure S2: Relaxed scan of S_1 state along asymmetric CH stretch using 2SA-MCSCF(8,9)/cc-pVDZ level of theory. The discontinuity in S_0 state is due to sudden change in optimized C= O bond lengths of the dication on S_1. The optimized C=O bond length changes from 1.24 Å at the C-H distance of 2.6 Å to 1.32 Å at the C-H distance of 2.9 Å. However, note that the S_1 state shows no discontinuity along the scan.

4 Dynamics with trajectory surface hopping (TSH)

Additional results on dynamics are shown in this section.

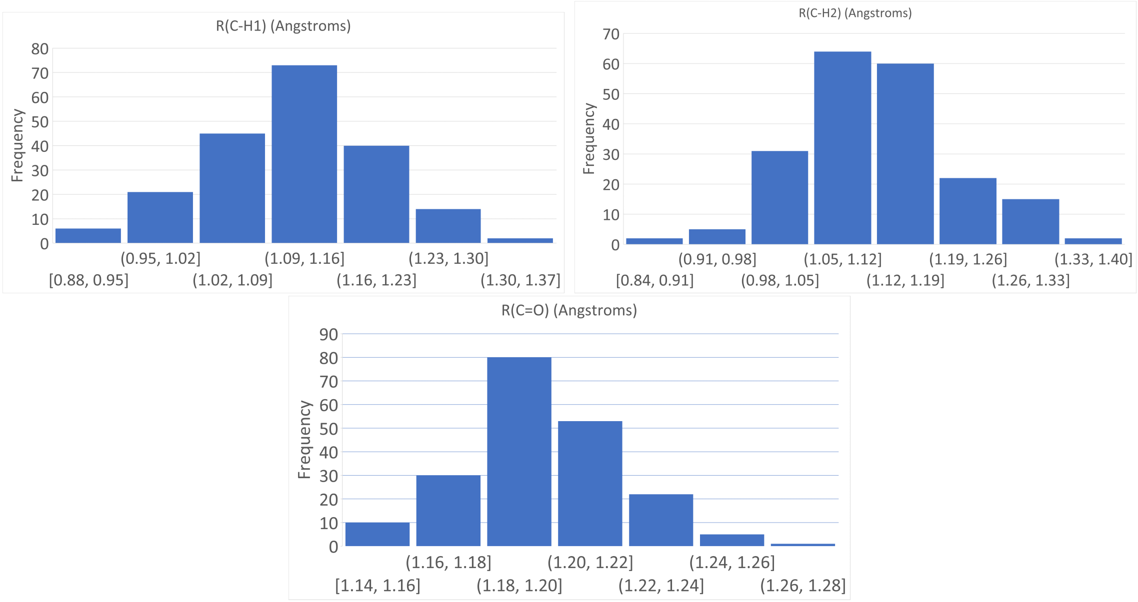

Figure S3: The C-Hs and C= O bond length distributions of 200 initial conditions produced with simple harmonic Wigner distribution.

Table S3: Summary of products (number of trajectories) produced from the trajectories ran on different electronic states with surface hopping. The channel with maximum number for each state is shown in red whereas the secondary major channels are shown in blue texts.

State	No. Traj.	Fail	H_2C^+ /O^+	CHO^+ /H^+	CO^+ /H/H^+	CO/H^+ /H^+/H^+	CO^+ /H_2^+	CH^+ /O^+/H	H_2CO^{2+}
S_0	200	46		147					7
S_1	200	54		16	1				129
S_2	200	50		26	92	11	2		19
S_3	200	58	100	10	12	3			17
S_4	200	43	64	15	45	31		1	1
S_5	200	40	134	6	15	5			

4.1 Plots of internal coordinates vs time for the trajectories ran on different states.

Refer to the main paper for the plots involving S_1 and S_2.

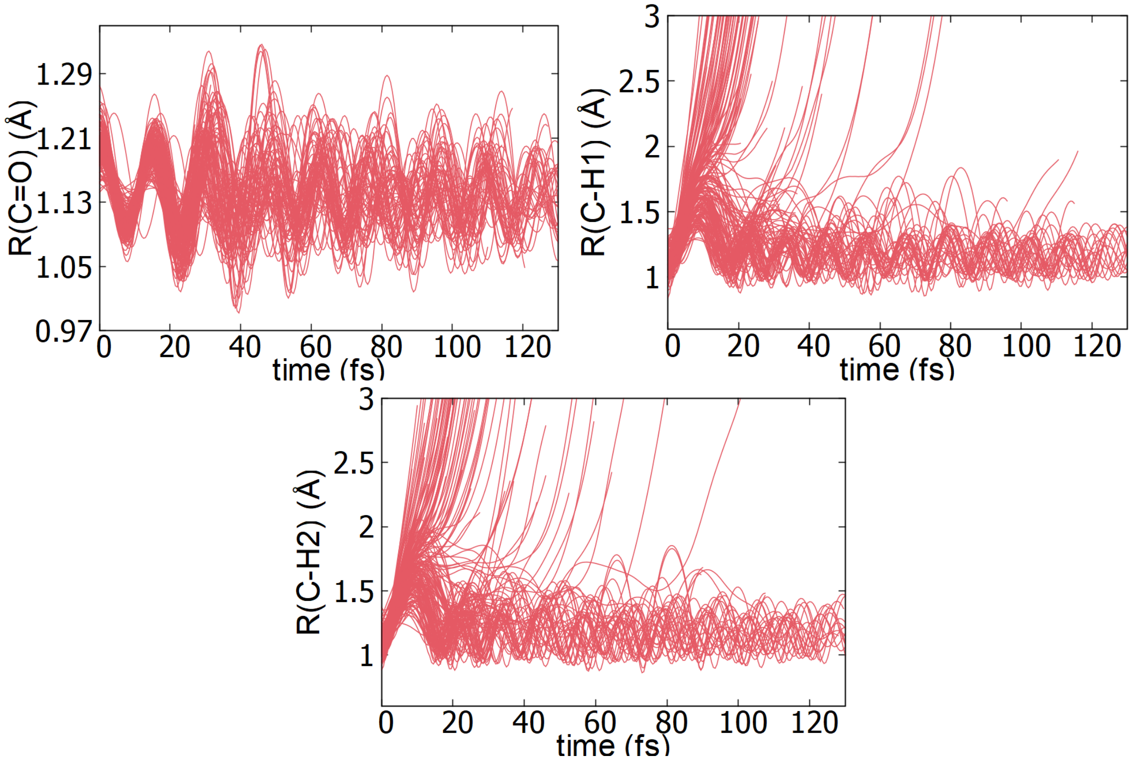

Figure S4: Plots of internal coordinates vs time for the dynamics ran on S_0.

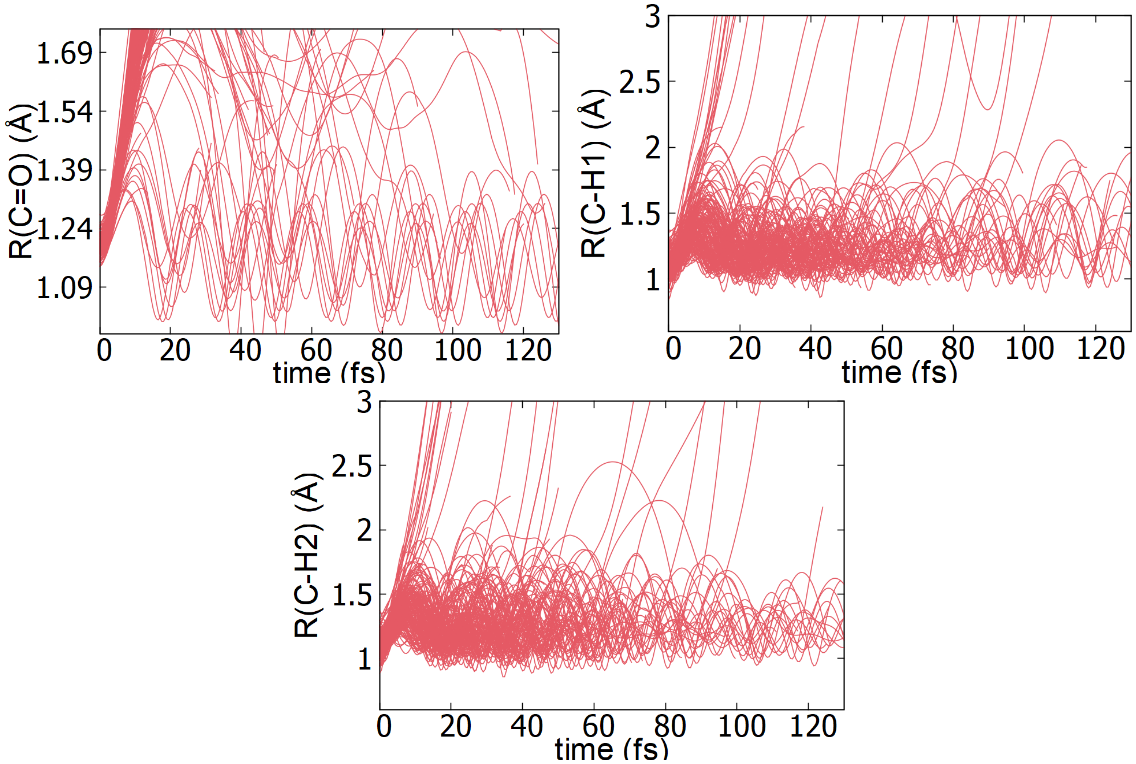

Figure S5: Plots of internal coordinates vs time for the dynamics ran on S_3.

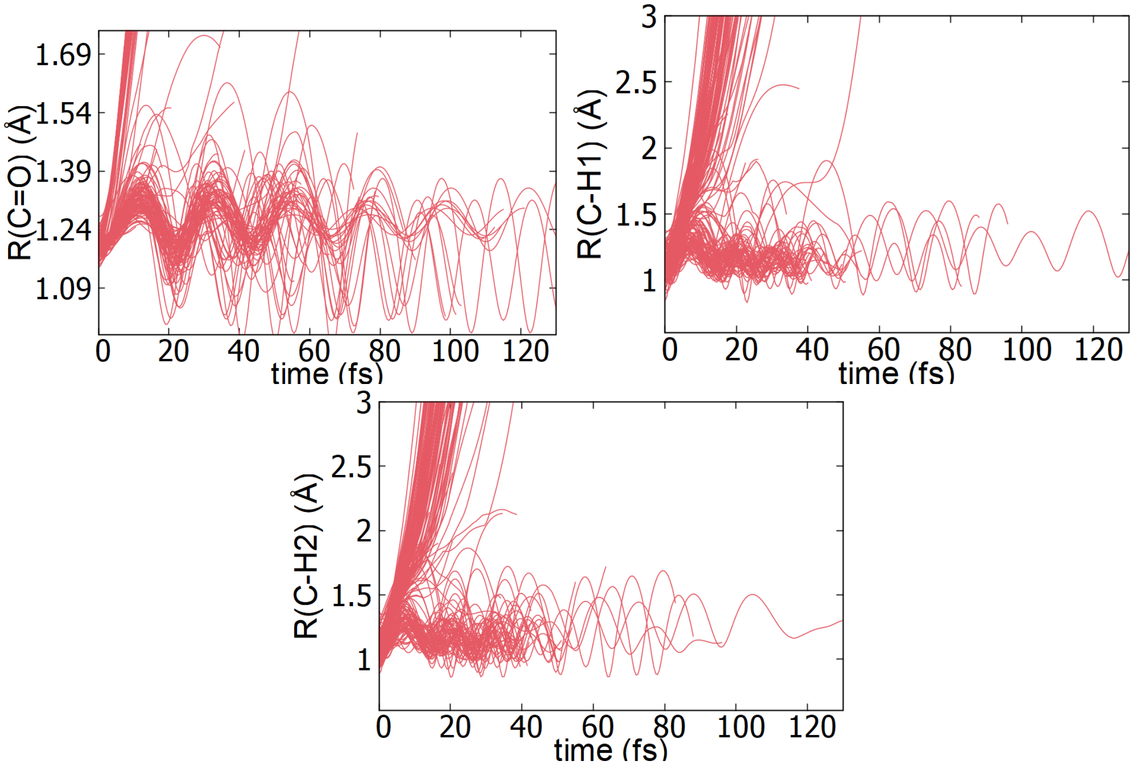

Figure S6: Plots of internal coordinates vs time for the dynamics ran on S_4.

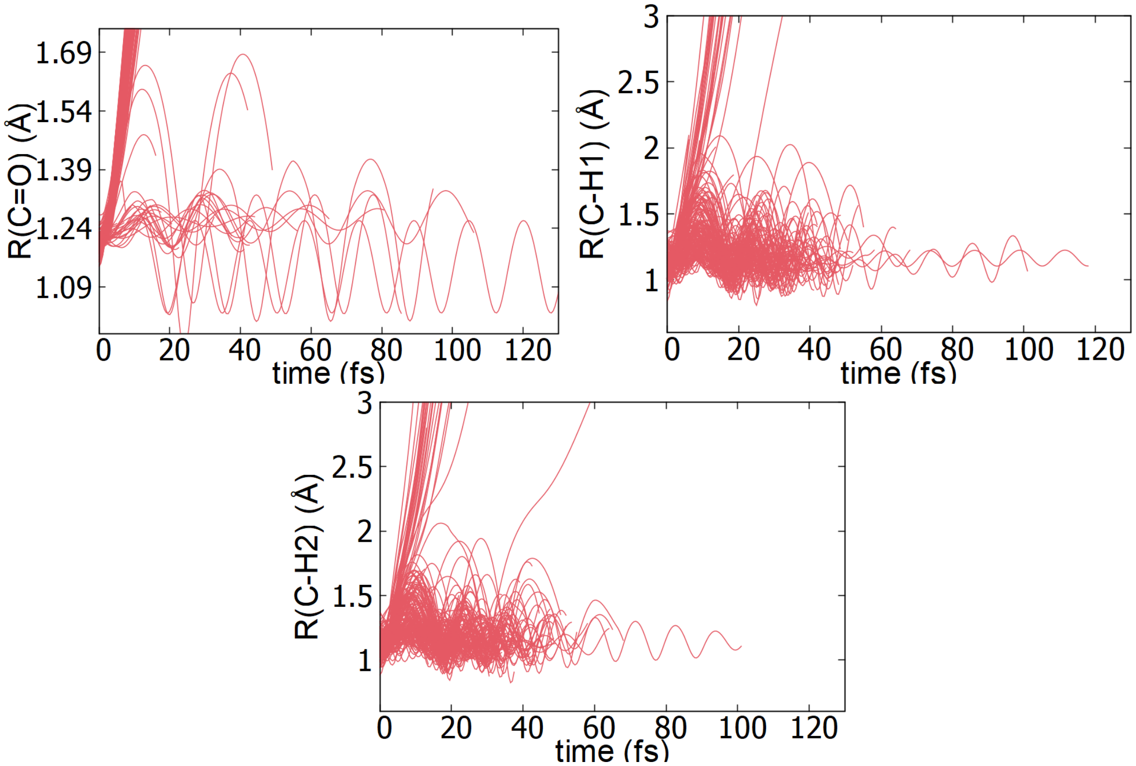

Figure S7: Plots of internal coordinates vs time for the dynamics ran on S_5.

4.2 Populations vs time for the trajectories ran on different states.

For the plots regarding S_1 and S_2, please refer to the main text.

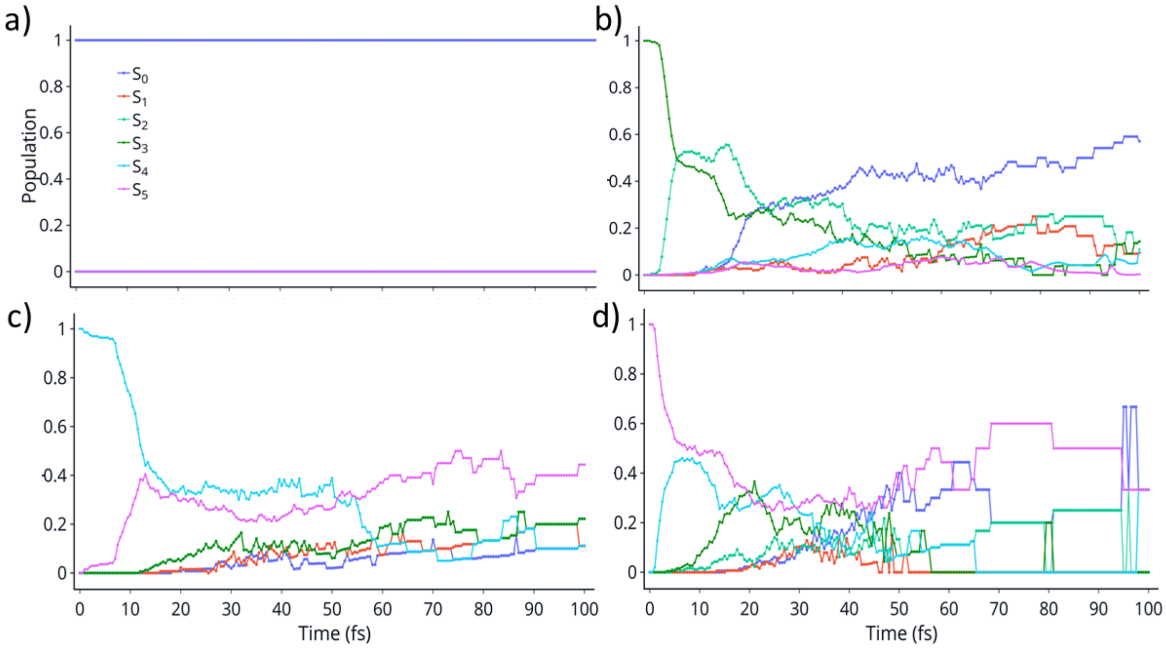

Figure S8: Plots of populations or trajectories on each state vs time for the dynamics ran on a) S_0, b) S_3, c) S_4, d) S_5.

5 State configurations

In order to better understand the symmetry of the states an orbital level diagram is shown for formaldehyde. The configurations for neutral formaldehyde and the states of the dication produced by removing two electrons are shown in Figure S9.

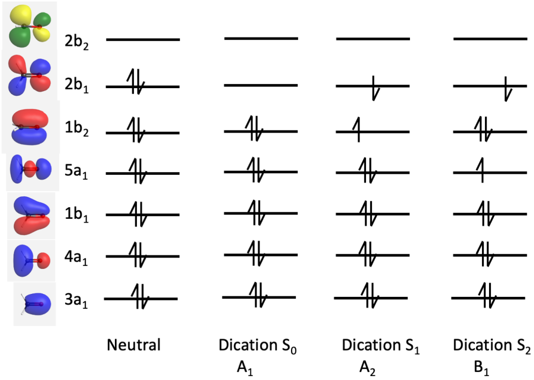

Figure S9: Orbital level diagram showing the configurations describing from the left: neutral formaldehyde, ground state of the dication, the first and the second excited states of the dication. The orbital shapes are shown on the left. Red and blue represent the positive and negative phases for occupied orbitals of the neutral, while yellow and green are used for the phases of the unoccupied orbitals.

6 Analysis of the trajectories initiated on S_2 and having asymmetric C-H stretch.

For the dynamics along S_1 wanted to examine whether there are trajectories that simultaneously stretch CO bond and are asymmetric, since in that case the S_1-S_0 gap could be small and there could be nonadiabatic coupling between the two states. We looked at the trajectories in more detail, and in particular examined trajectories that started with asymmetric CH stretches. We monitored the C=O bond lengths, the S_0 S_1 energies and whether hoppings occur. The results for representative trajectories are shown in Figure S10. In summary, what we observe is that the S_1-S_0 gap is determined by the C=O stretch, and it becomes very small when the bond is greater than 1.6 Å. Even in that case however we do not see

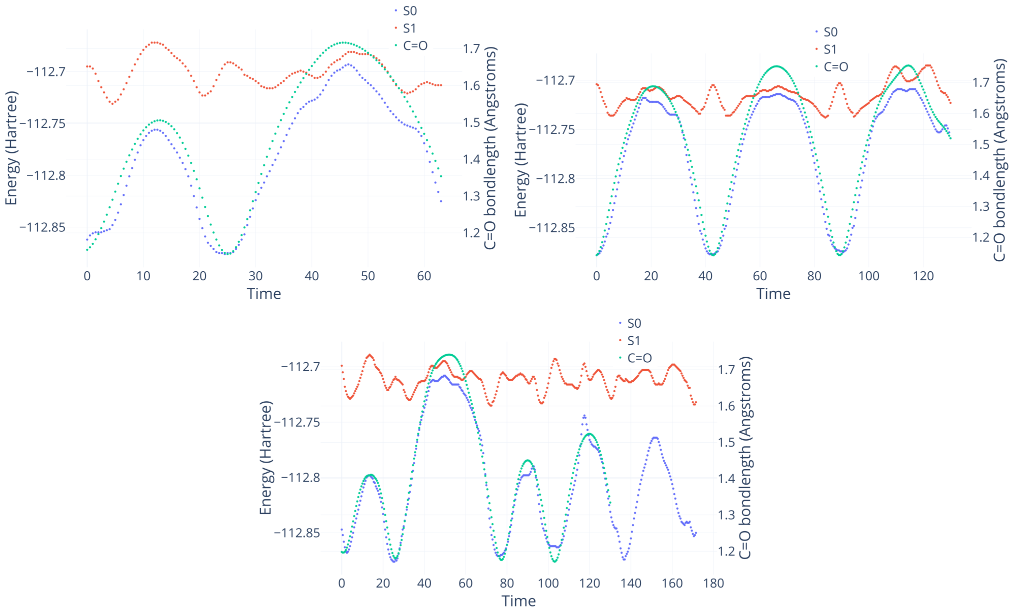

Figure S10: Plots of C=O stretch, and S_0 and S_1 energies for the few trajectories where C=O bond lengths were found to be greater than 1.6 Angstroms. It can be clearly seen that the S_0 and S_1 are closer in energies only when C=O bond length is greater than 1.6 Å.

any hops to the ground state. This indicates that the nonadiabatic coupling between S_1 and S_0 is still negligible although the energy gap between these states is small. This is likely because the asymmetry remains small (the C-H bond lengths do not differ by more than 0.1 to 0.2 Å), so the coupling is still small.