Electronic Supplementary Information

Curve Crossing in a Manifold of Coupled Electronic States: Direct Quantum Dynamics Simulations of Formamide

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1 Structures

C	-0.022639	0.128508	0.009546
N	1.341656	0.147491	0.115219
H	1.825170	1.029436	0.075846
H	1.773750	-0.592042	0.648172
O	-0.726000	-0.810878	0.306816
H	-0.433844	1.060410	-0.421596

Table S1: Formamide optimised at the CCSD/6-311+G* level of theory. C_1 symmetry.

C	-0.000003	0.000000	-0.008254
N	-0.000910	0.000000	1.354098
O	0.994848	0.000000	-0.700139
H	-1.018906	0.000000	-0.438558
H	-0.857392	0.000000	1.879293
H	0.875945	0.000000	1.849650

Table S2: Formamide optimised at the CCSD/6-311+G* level of theory. C_s symmetry.

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.345244
N	1.075869	0.000000	-0.672382
H	0.876130	0.000000	-1.669171
H	0.922051	0.000000	1.635417
H	-1.022339	0.000000	-0.385759

Table S3: Formimidic acid optimised at the CCSD/6-311+G* level of theory. C_s symmetry.

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C	-0.047200	0.000000	0.089408
O	-0.025241	0.000000	1.369435
N	1.178869	0.000000	-0.350543
H	-0.974782	0.000000	-0.484026
H	1.452117	0.000000	-1.324615
H	1.263645	0.000000	0.999811

Table S4: Transition state between formamide and formimidic acid optimised at the CCSD/6-311+G* level of theory. C_s symmetry.

2 Normal Modes

Tables S5 and S6 show the nomal mode vectors for formamide and formimidic acid, respectively, calculated at the SA8-CAS(10,8)/6-31G* level of theory. These are the coordinates used in the direct dynamics simulations.

Table S5: Normal modes of formamide calculated at the SA8-CAS(10,8)/6-31G* level of theory at the optimised C_s structure. It should be noted that the arrow representing the CH stretching mode (ν_{10}) has been reduced in scale by 40%.

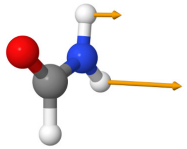
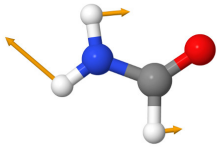
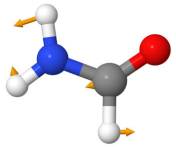
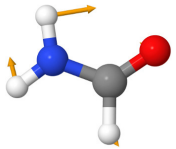
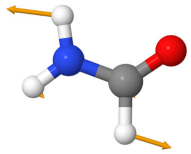
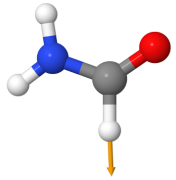
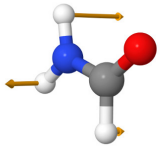
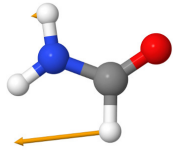
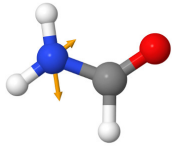
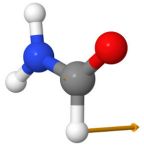
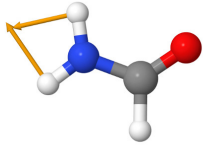
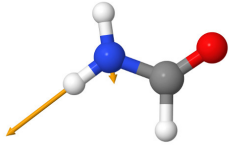
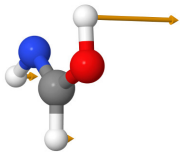
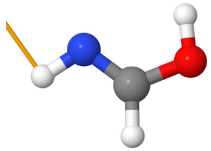
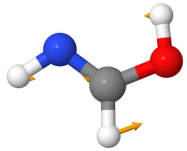
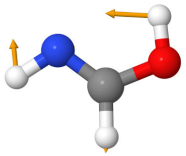
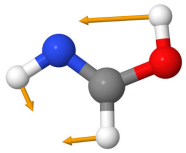
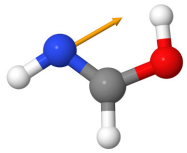
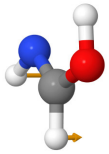
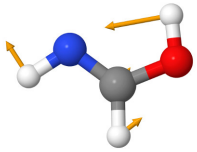
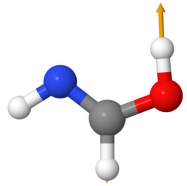
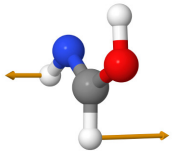
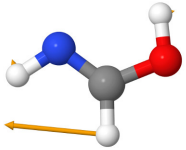
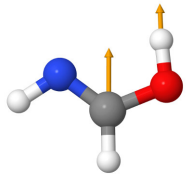
Label		Freq. (cm^{-1})	Label		Freq. (cm^{-1})	Label		Freq. (cm^{-1})
$\nu_1(A'')$		320.66i	$\nu_5(A')$		1108.68	$\nu_9(A')$		2031.85
$\nu_2(A')$		598.06	$\nu_6(A')$		1356.26	$\nu_{10}(A')$		2640.00
$\nu_3(A'')$		601.74	$\nu_7(A')$		1397.43	$\nu_{11}(A')$		3855.27
$\nu_4(A'')$		1014.98	$\nu_8(A')$		1803.58	$\nu_{12}(A')$		4029.16

Table S6: Normal modes of formimidic calculated at the SA8-CAS(10,8)/6-31G* level of theory at the optimised C_s structure. It should be noted that the arrow representing the OH stretching mode has been reduced in scale by 40%.

Label		Freq. (cm^{-1})	Label		Freq. (cm^{-1})	Label		Freq. (cm^{-1})
$\nu_1(A'')$		630.43	$\nu_5(A')$		1150.16	$\nu_9(A')$		1854.47
$\nu_2(A')$		635.19	$\nu_6(A')$		1284.95	$\nu_{10}(A')$		3126.07
$\nu_3(A'')$		911.91	$\nu_7(A')$		1447.58	$\nu_{11}(A')$		3379.82
$\nu_4(A'')$		1062.53	$\nu_8(A')$		1515.33	$\nu_{12}(A')$		3449.48

3 Excited States

Figures S1 and S2 show the results from a set of calculations on formamide and formamidic acid, respectively, at the SA8-CAS(10,8)/6-31G* level of theory.
The column titles at the top of the page, SA3, SA4, SA5, and so-on refer to the total number of states included in the calculation where, for example, "SA3" means that this column represents a State Averaged calculation over a total of 3 states, including the ground state. These column titles refer to both the top and bottom sections of the figure.
The top section of the figure contains the information pertaining to the characterisation of the orbitals included in the active space. In this section the text above the dotted line lists a simplified characterisation of the occupied orbitals, whilst the text below the dotted line refers to the virtual orbitals. We call this the *active space characterisation section*. This simplification has been made so as to decrease the complexity of the data table.
The bottom section of this figure is called the *excited state characterisation section*, which summarises four key pieces of information. The first line is the calculated energy of the S_0 state in the relevant state averaged calculations. The numbers in the rows below are the excitation energies, in eV, from the relevant S_0 state to the excited state, hence the first row of numbers below the S_0 energy is the S_1, the second row is the S_2, and so on.
The coloured boxes below the excitation energies are the characterisations of the principal transition(s) contributing to the excitation, where the box on the left characterises the orbital from which the excitation occurs, and the box on the right characterises the orbital into which the electron is excited. In some instances, more than one type of excitation significantly contributes to the overall character of the state. In these cases the numerical values were considered and the two or three most significant, listed in order, are included. It was considered that the emphasis in this type of analysis should be in the characterisation so while the numerical values are available, they have not been included. The explanation of the colours of the transitions are listed in a key to the right of the active space characterisation.
The final piece of information included in the excited-state characterisation are where the numbers of the excitation energies are written in red. These correspond to the states with an oscillator strength greater than 0.01. As with the transitions, the numerical values of these oscillator strengths are available though have not been included for simplicity.

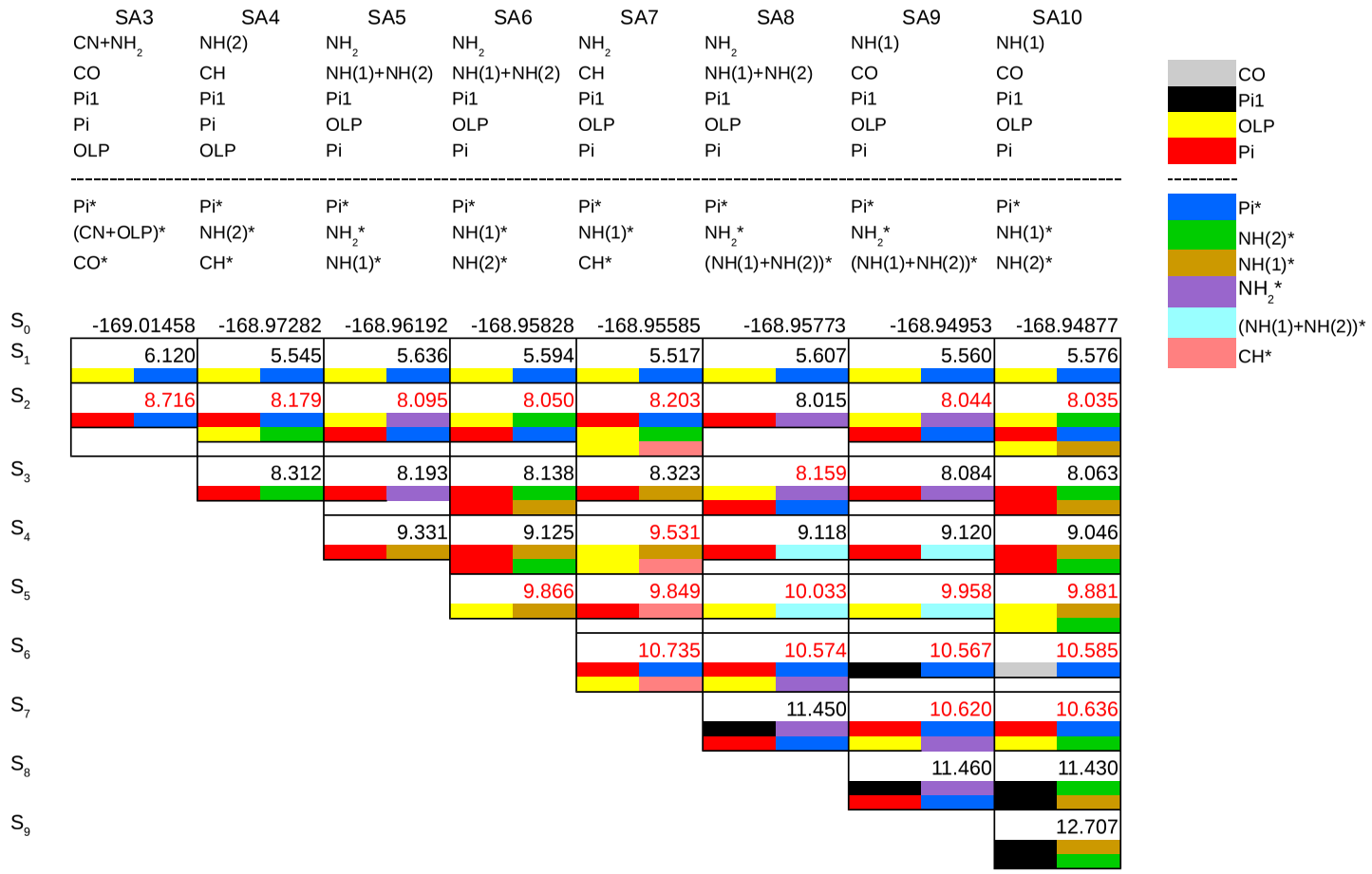


Figure S1: Character of MOs for formamide using a SA-CAS(10,8) with different numbes of states. Each cell represents a state with excitation energy (in eV) relative to the ground-state (energy in Hartree). The coloured boxes relate to the character of the main configurations with an electron being promoted from the left to the right box. Key to colours on the right hand side. The list of orbitals above the cells list those in the CAS space. Numbers in red are for states with significant oscillator strength (> 0.01).

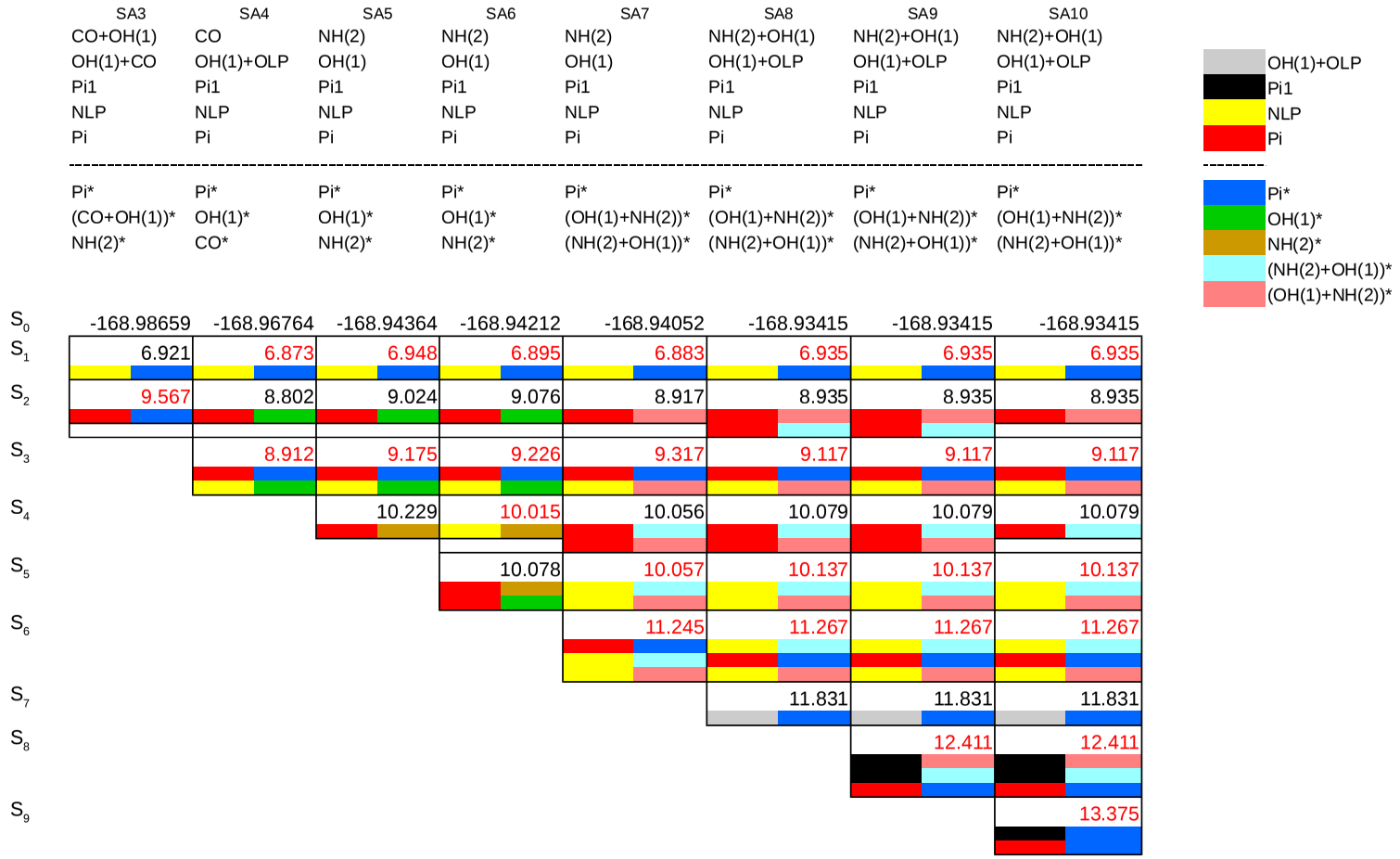
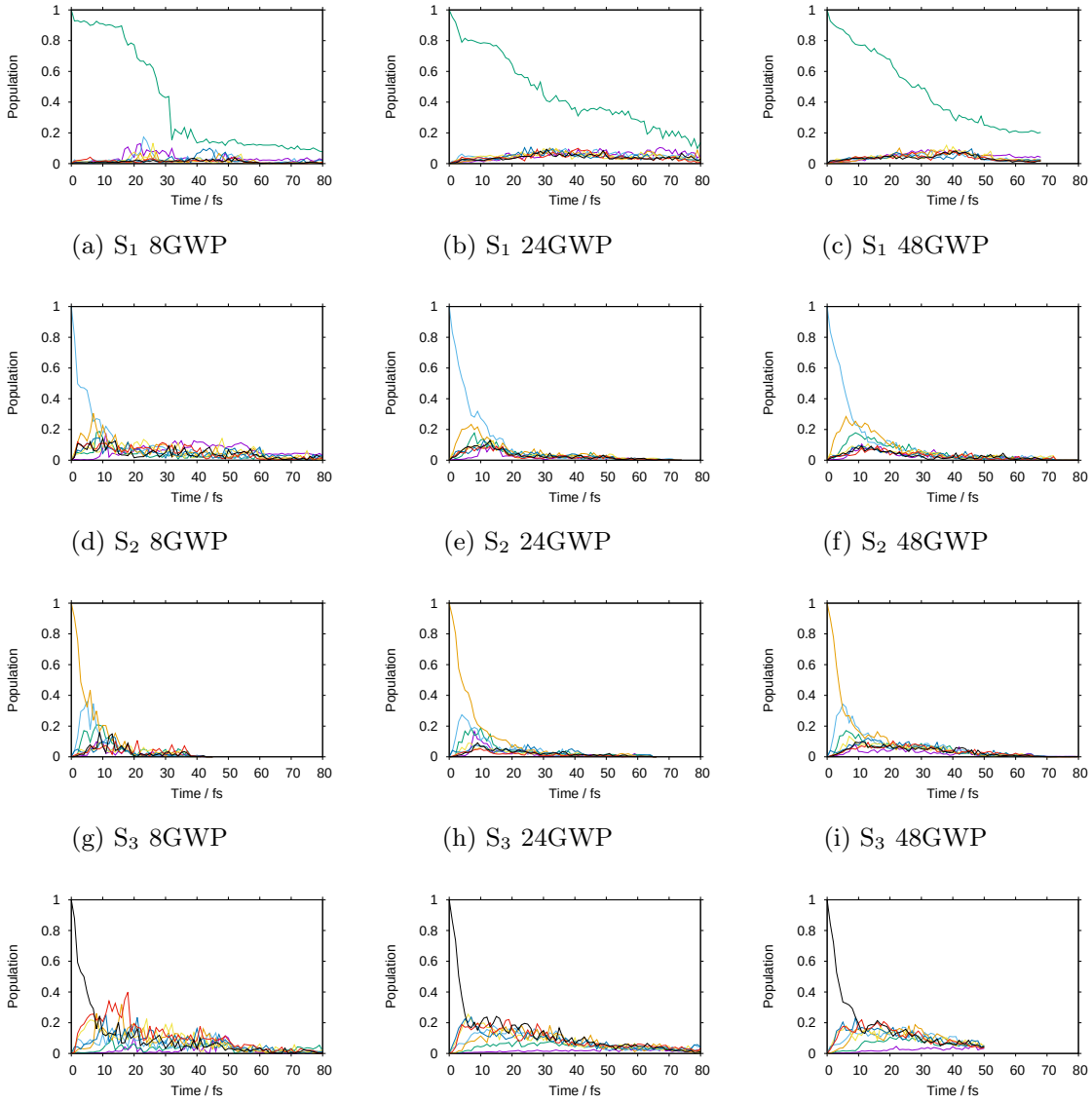


Figure S2: Character of MOs for formimidic acid using a SA-CAS(10,8) with different numbers of states. Each cell represents a state with excitation energy (in eV) relative to the ground-state (energy in Hartree). The coloured boxes relate to the character of the main configurations with an electron being promoted from the left to the right box. Key to colours on the right hand side. The list of orbitals above the cells list those in the CAS space. Numbers in red are for states with significant oscillator strength (> 0.01).



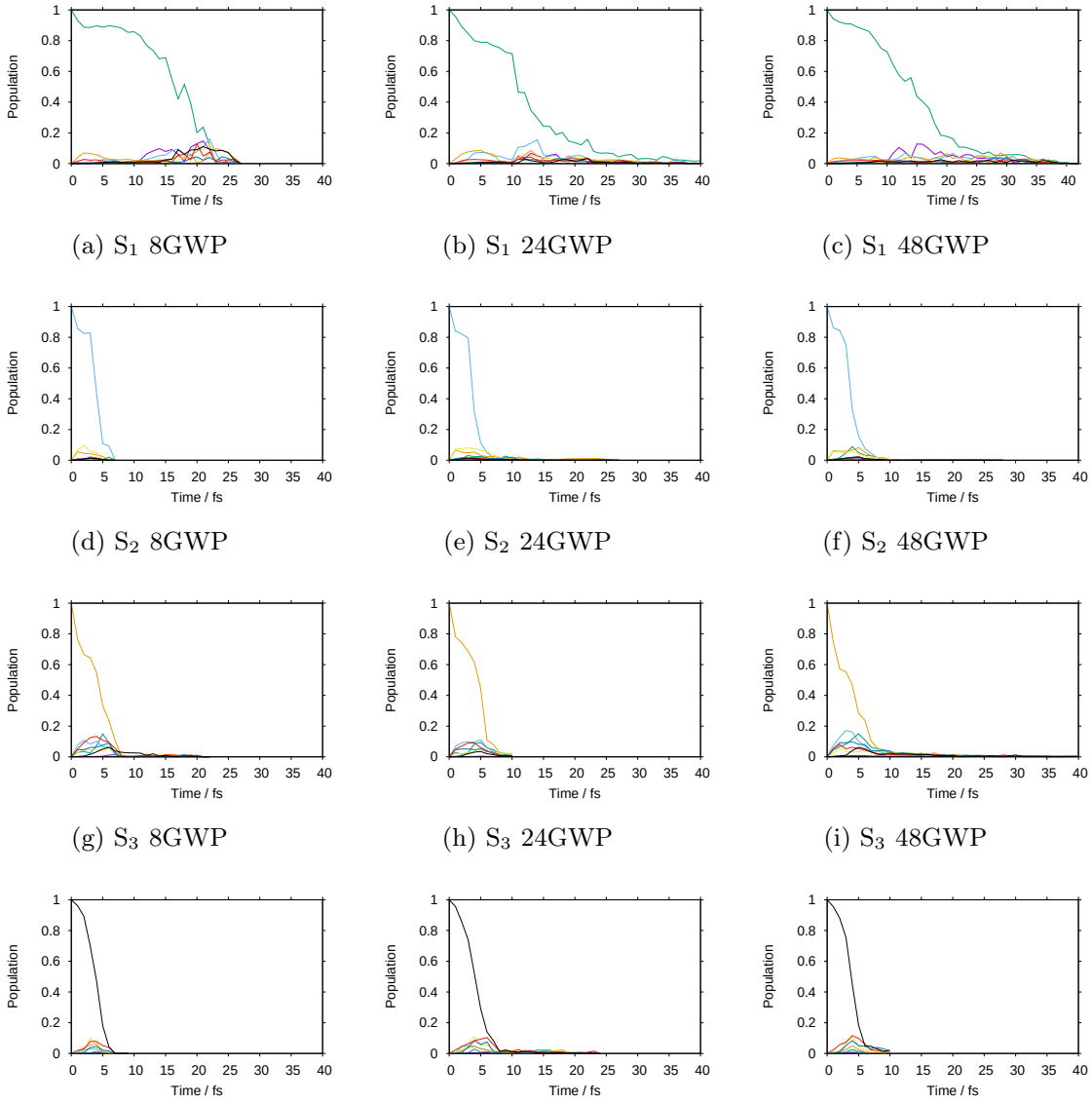
(a) S_1 8GWP (b) S_1 24GWP (c) S_1 48GWP

(d) S_2 8GWP (e) S_2 24GWP (f) S_2 48GWP

(g) S_3 8GWP (h) S_3 24GWP (i) S_3 48GWP

(j) S_7 8GWP (k) S_7 24GWP (l) S_7 48GWP

Figure S3: Diabatic state populations from DD-vMCG simulations of formamide starting with a vertical excitation to various states and using various numbers of GWPs. Key: S_0: purple; S_1: green; S_2: light blue; S_3: orange; S_4: yellow; S_5: dark blue; S_6: red; S_7: black.



(a) S_1 8GWP (b) S_1 24GWP (c) S_1 48GWP

(d) S_2 8GWP (e) S_2 24GWP (f) S_2 48GWP

(g) S_3 8GWP (h) S_3 24GWP (i) S_3 48GWP

(j) S_7 8GWP (k) S_7 24GWP (l) S_7 48GWP

Figure S4: Diabatic state populations from DD-vMCG simulations of formimidic acid starting with a vertical excitation to various states and using various numbers of GWPs. Key: S_0: purple; S_1: green; S_2: light blue; S_3: orange; S_4: yellow; S_5: dark blue; S_6: red; S_7: black.