Roaming Wavepacket in the Dynamics of Electronically Excited 2-Hydroxypyridine - Supplementary Materials

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Table 1 CASSCF and MS-CASPT2 relative energies using $(8e,7o)$ and $(10e,8o)$ active spaces. All energies are given in eV relative to the ground-state energy.

State	CASSCF (8,7)	CASSCF (10,8)	MS-CASPT2 (8,7)	MS-CASPT2 (10,8)
$S_0(1^1A')$ C_s equilibrium geometry (minimum)				
$1^1A'$	0	0	0	0
$2^1A'$	5.128	5.099	4.841	4.776
$1^1A''$	5.942	5.945	5.566	5.574
$S_1(2^1A'-\pi,\pi^\star)$ C_s equilibrium geometry (minimum)				
$1^1A'$	0.241	0.240	0.162	0.161
$2^1A'$	4.853	4.827	4.539	4.475
$1^1A''$	5.990	5.999	5.620	5.634
$S_1(1^1A''-n,\pi^\star)$ C_s equilibrium geometry (saddle point)				
$1^1A'$	0.691	0.691	0.652	0.651
$2^1A'$	5.567	5.543	5.307	5.249
$1^1A''$	5.225	5.228	5.034	5.042

Table 2 CASSCF(6,6)/cc-pVTZ optimized cartesian coordinates for S_0 minimum (see Fig. 1a)

atom	x (Å)	y (Å)	z (Å)
C	-1.2385077362	-0.9858320893	0.0000000000
C	-0.1356639499	-1.8133333143	0.0000000000
C	1.1326985105	-1.2218404086	0.0000000000
C	1.2309621477	0.1523409633	0.0000000000
C	0.0393611861	0.8896601127	0.0000000000
N	-1.1514069882	0.3509661475	0.0000000000
O	0.1271849060	2.2285652881	0.0000000000
H	-2.2325787816	-1.3898465544	0.0000000000
H	-0.2550793278	-2.8782994918	0.0000000000
H	2.0180293863	-1.8279659975	0.0000000000
H	2.1719646270	0.6634699084	0.0000000000
H	-0.7460955596	2.5839959261	0.0000000000

Table 3 CASSCF(6,6)/cc-pVTZ optimized cartesian coordinates for $S_1(\pi,\pi^\star)$ minimum (see Fig. 1b)

atom	x (Å)	y (Å)	z (Å)
C	-1.2385077362	-0.9858320893	0.0000000000
C	-0.1356639499	-1.8133333143	0.0000000000
C	1.1326985105	-1.2218404086	0.0000000000
C	1.2309621477	0.1523409633	0.0000000000
C	0.0393611861	0.8896601127	0.0000000000
N	-1.1514069882	0.3509661475	0.0000000000
O	0.1271849060	2.2285652881	0.0000000000
H	-2.2325787816	-1.3898465544	0.0000000000
H	-0.2550793278	-2.8782994918	0.0000000000
H	2.0180293863	-1.8279659975	0.0000000000
H	2.1719646270	0.6634699084	0.0000000000
H	-0.7460955596	2.5839959261	0.0000000000

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Table 4 CASSCF(8,7)/cc-pVTZ optimized cartesian coordinates for $S_1(n,\pi^\star)$ saddle point (see Fig. 1c)

atom	x (Å)	y (Å)	z (Å)
C	-1.2741354998	-0.9723453801	0.0000000000
C	-0.1253431204	-1.8262657150	0.0000000000
C	1.1861334428	-1.2653906944	0.0000000000
C	1.2545406801	0.1667758915	0.0000000000
C	0.0426731111	0.9030864491	0.0000000000
N	-1.2095985169	0.3841153446	0.0000000000
O	0.1237271061	2.2340985020	0.0000000000
H	-2.2568605982	-1.3981905950	0.0000000000
H	-0.2738284923	-2.8871721366	0.0000000000
H	2.0639899427	-1.8739966204	0.0000000000
H	2.1810019904	0.7008675135	0.0000000000
H	-0.7514316256	2.5862979309	0.0000000000

Table 5 SA2-CASSCF(8,7)/cc-pVTZ optimized cartesian coordinates for S_1/S_2 MECI (see Fig. 1d)

atom	x (Å)	y (Å)	z (Å)
C	-1.2901211565	-1.0425846692	0.0000000000
C	-0.1473707883	-1.8356013110	0.0000000000
C	1.1414529264	-1.2469879904	0.0000000000
C	1.2518176339	0.1925280805	0.0000000000
C	0.1031149140	0.9432126488	0.0000000000
N	-1.1110762551	0.3240364365	0.0000000000
O	0.1150087246	2.2817232031	0.0000000000
H	-2.2904648117	-1.4145732477	0.0000000000
H	-0.2638703183	-2.9012307768	0.0000000000
H	2.0196743866	-1.8568854392	0.0000000000
H	2.1976540602	0.6929767014	0.0000000000
H	-0.7649508958	2.6152668543	0.0000000000

Table 6 CASSCF(8,7)/cc-pVTZ optimized cartesian coordinates for $S_1(n,\pi^\star)$ minimum (see Fig. 1e)

atom	x (Å)	y (Å)	z (Å)
C	-1.2911201811	-1.0654678938	0.0314696057
C	-0.1574745660	-1.8368437865	-0.0103627327
C	1.1195860106	-1.2374919746	0.0679863797
C	1.2386470127	0.2120513660	0.0237215368
C	0.1182855885	0.9567958781	0.1016074793
N	-1.0562283924	0.2736205919	0.2886500863
O	0.0745457697	2.2957580905	0.0818967355
H	-2.2966138545	-1.4012324787	-0.0897908973
H	-0.2586061957	-2.8957056407	-0.1484090223
H	2.0012008080	-1.8421850359	0.0289355483
H	2.1778711676	0.6980311946	-0.1433952564
H	-0.7092247469	2.5945501790	-0.3473094629

Table 7 CASSCF(8,7)/cc-pVTZ optimized cartesian coordinates for S_1 transition state TS_1 (see Fig. 1f)

atom	x (Å)	y (Å)	z (Å)
C	-1.2922360412	-1.0166962079	-0.0764022297
C	-0.1429021635	-1.8159608453	-0.0842595073
C	1.1393370324	-1.2436292860	0.0597510255
C	1.2596547928	0.1917855335	0.1366323919
C	0.0943183291	0.9321864856	0.1073882180
N	-1.1062790226	0.3210993724	0.1870212453
O	0.1136767585	2.2596581908	-0.0442945995
H	-2.2743545232	-1.4136076977	0.0645621758
H	-0.2658505471	-2.8806709567	-0.1215631607
H	2.0149738346	-1.8569409084	0.0182897436
H	2.1825808107	0.6911940097	-0.0783934537
H	-0.7620512604	2.5834633098	-0.1687328492

Table 8 MS-CASPT2(8,7)/cc-pVTZ optimized cartesian coordinates for S_0 minimum (see Fig. 1a)

atom	x (Å)	y (Å)	z (Å)
C	-1.2411487518	-0.9777622782	0.0000000000
C	-0.1346502795	-1.8139521935	0.0000000000
C	1.1332292054	-1.2248612581	0.0000000000
C	1.2403202586	0.1552701046	0.0000000000
C	0.0504537844	0.8951600594	0.0000000000
N	-1.1644459655	0.3644994752	0.0000000000
O	0.1395654512	2.2422307538	0.0000000000
H	-2.2415634910	-1.3884596354	0.0000000000
H	-0.2590729184	-2.8855811463	0.0000000000
H	2.0233456447	-1.8365047338	0.0000000000
H	2.1898950711	0.6663203108	0.0000000000
H	-0.7750595888	2.5555210318	0.0000000000

Table 9 MS-CASPT2(8,7)/cc-pVTZ optimized cartesian coordinates for $S_1(\pi,\pi^\star)$ minimum (see Fig. 1b)

atom	x (Å)	y (Å)	z (Å)
C	-1.2701269183	-0.9528891672	0.0000000000
C	-0.1221966134	-1.8026691506	0.0000000000
C	1.1920190076	-1.2688601756	0.0000000000
C	1.2640498835	0.1641006248	0.0000000000
C	0.0510466363	0.8969583446	0.0000000000
N	-1.2319210837	0.4114521315	0.0000000000
O	0.1379084859	2.2234473867	0.0000000000
H	-2.2546250108	-1.3988027969	0.0000000000
H	-0.2851861136	-2.8707307219	0.0000000000
H	2.0699924832	-1.8906113901	0.0000000000
H	2.1932622147	0.7114897245	0.0000000000
H	-0.7833545513	2.5289956803	0.0000000000

Table 10 MS-CASPT2(8,7)/cc-pVTZ optimized cartesian coordinates for $S_1(n,\pi^\star)$ saddle point minimum (see Fig. 1c)

atom	x (Å)	y (Å)	z (Å)
C	-1.3140031896	-1.0570214849	0.0000000000
C	-0.1355535469	-1.8255378074	0.0000000000
C	1.1212214746	-1.2456415242	0.0000000000
C	1.2685566626	0.1978500927	0.0000000000
C	0.1180654230	0.9506207033	0.0000000000
N	-1.0371132626	0.2909841850	0.0000000000
O	0.1155182316	2.2997230779	0.0000000000
H	-2.3285451753	-1.4083426863	0.0000000000
H	-0.2612322829	-2.8993272970	0.0000000000
H	1.9993863997	-1.8707668578	0.0000000000
H	2.2134370098	0.7158210703	0.0000000000
H	-0.7988693240	2.6035190183	0.0000000000

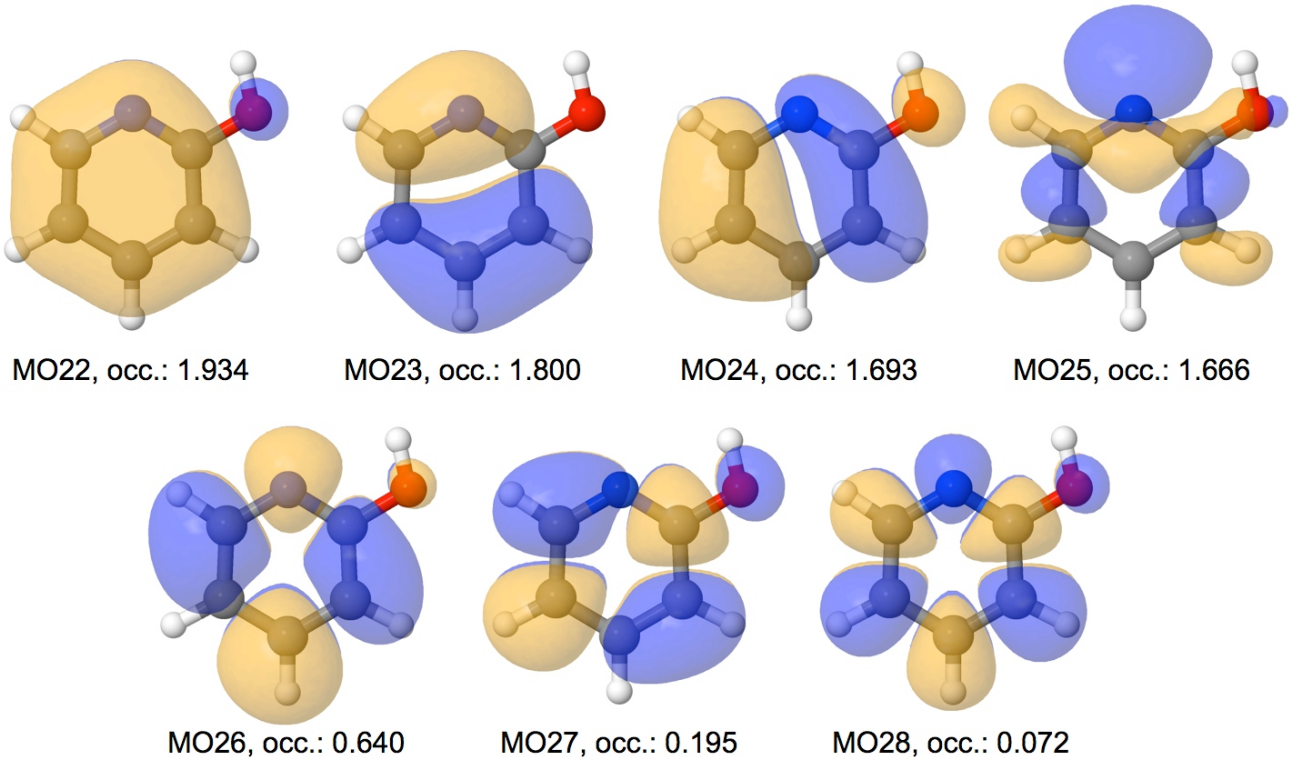
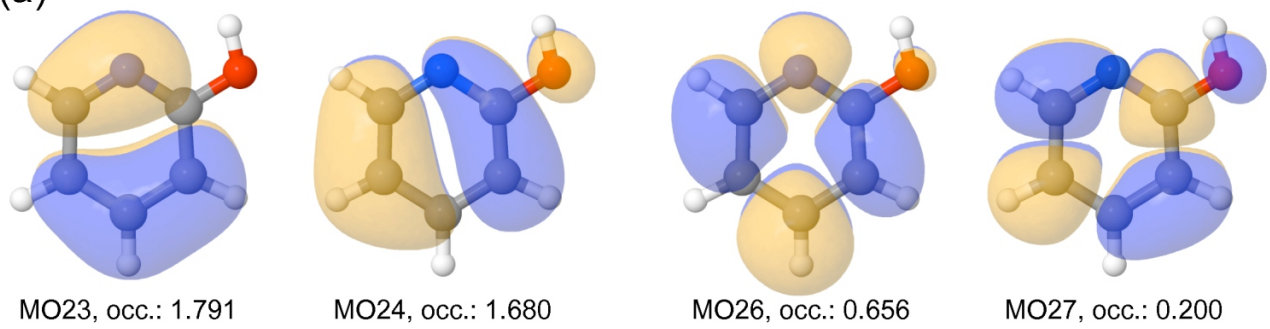


Fig. 1 SA3-CASSCF(8,7)/cc-pVTZ active orbitals and corresponding fractional occupations at the S_0 minimum geometry

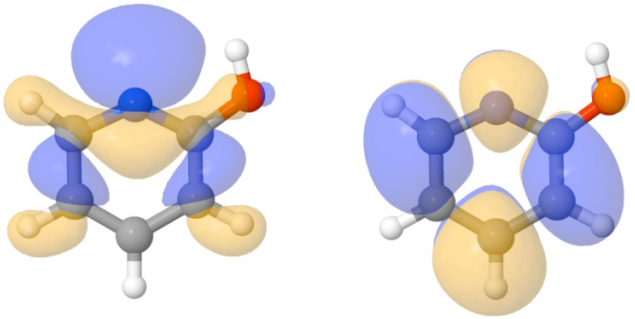
(a)



MO23, occ.: 1.791 MO24, occ.: 1.680 MO26, occ.: 0.656 MO27, occ.: 0.200

$$\Psi^{\mathrm{CASSCF}}_{S_1(\pi,\pi^*)} = 0.739\phi_{24\rightarrow 26} - 0.469\phi_{23\rightarrow 27}$$

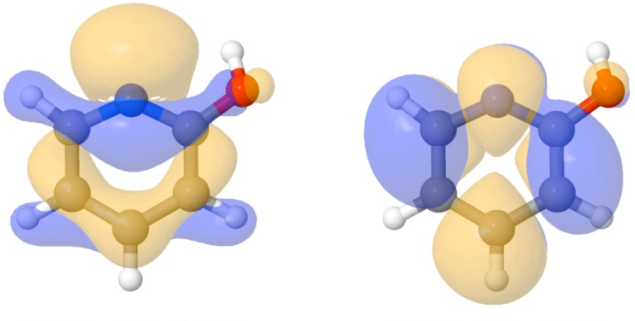
(b)



MO25, occ.: 1.666 MO26, occ.: 0.648

$$\Psi^{\mathrm{CASSCF}}_{S_1(n,\pi^*)} = 0.905\phi_{25\rightarrow 26}$$

(c)



MO25, occ.: 1.644 MO26, occ.: 0.651

$$\Psi^{\mathrm{CASSCF}}_{S_1(n,\pi^*)} = 0.852\phi_{25\rightarrow 26}$$

Fig. 2 SA3-CASSCF(8,7)/cc-pVTZ main configurations for (a) $S_1(\pi,\pi^\star)$ minimum, (b) $S_1(n,\pi^\star)$ SP, and (c) $S_1(n,\pi^\star)$ minimum. Natural orbitals, corresponding fractional occupations and main configurations ϕ are given at the respective CASSCF/cc-pVTZ optimized geometries.