

***Electronic Supplementary Information (ESI)***

***Photolytic mechanisms of hydroxylamine***

by

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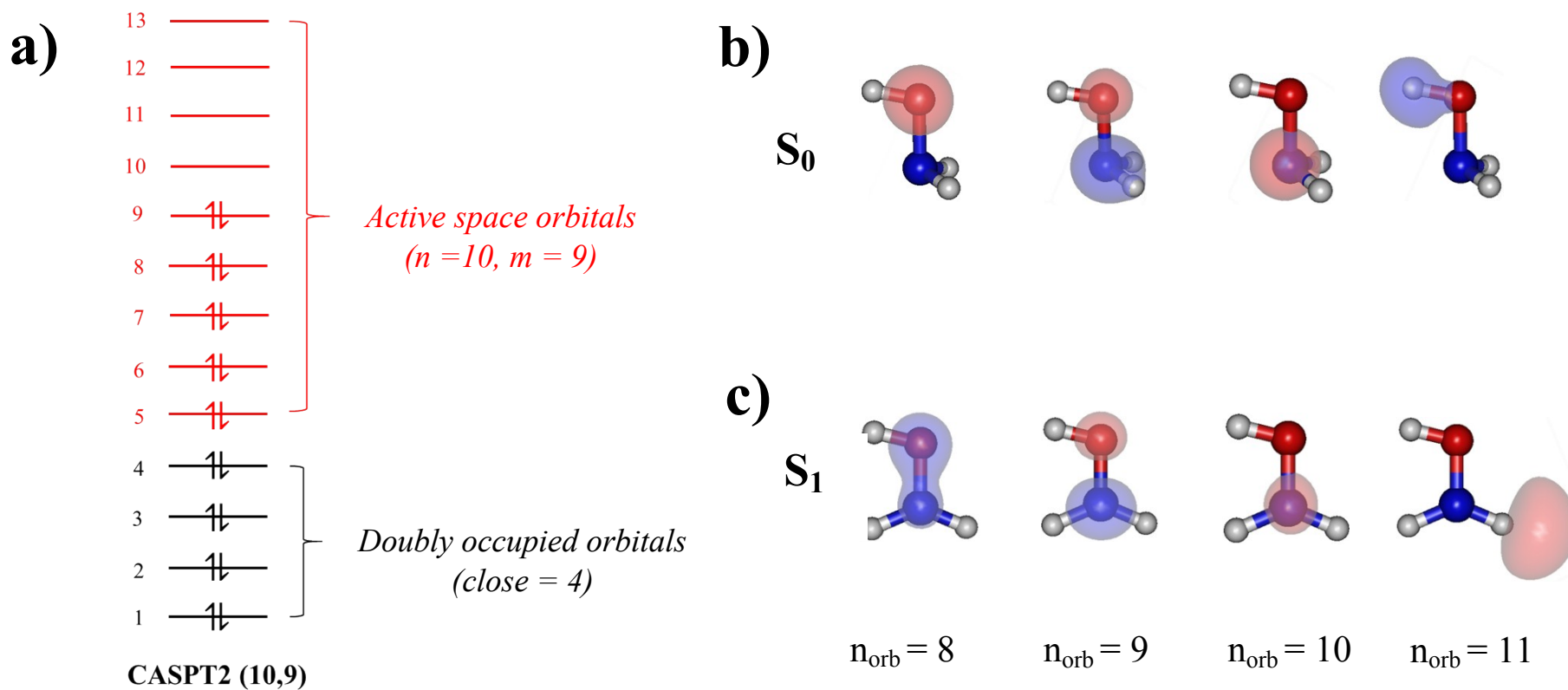
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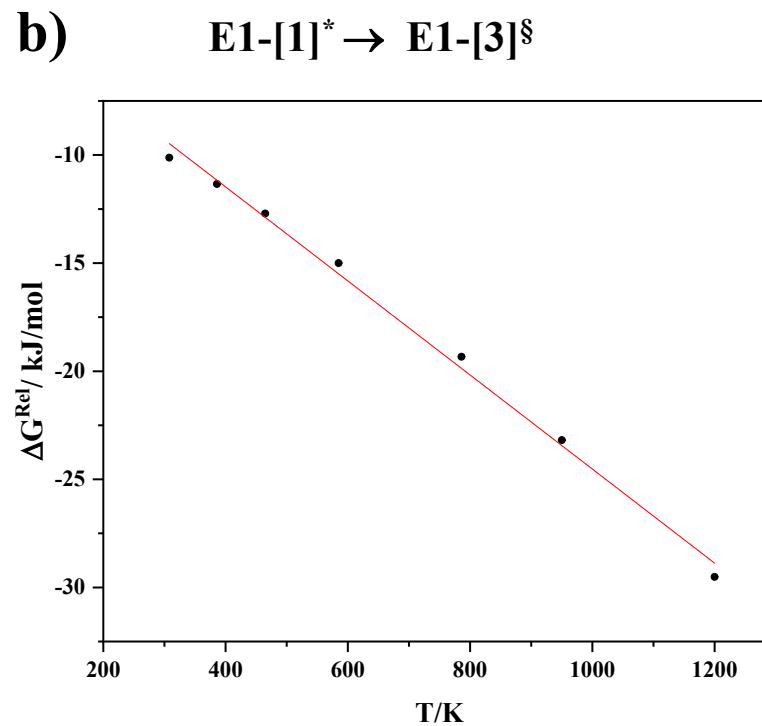
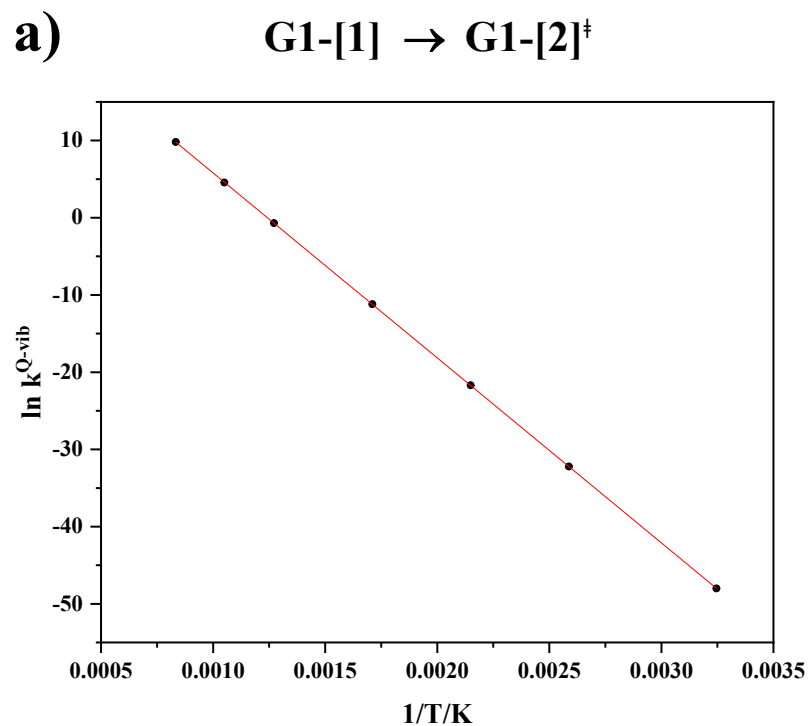
**Figure S1** a) Schematic diagram showing doubly occupied and active spaces used in CASPT2(10,9) calculations.

b)-c) Spatial distributions of the orbitals potentially involved in  $S_0 \rightarrow S_1$  excitation of  $\text{NH}_2\text{OH}$ .



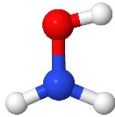
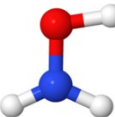
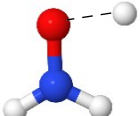
**Figure S2** a) Linear relationship between  $\ln k^{Q\text{-vib}}$  and  $1/T$  used in the calculations of the enthalpy of activation ( $\Delta H^\ddagger$ ) for formation of the precursor in the  $S_0$  state (structure **G1-[2]<sup>‡</sup>** in channel (1)).

b) Linear relationship between  $\Delta G^{\text{Rel}}$  and  $T$  used in the calculation of the enthalpy of the exothermic process ( $\Delta H^{\text{Rel}}$ ) in the  $S_1$  state (**E1-[1]<sup>\*</sup> → E1-[3]<sup>§</sup>**).



**Figure S2a-b**

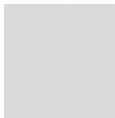
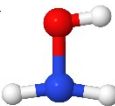
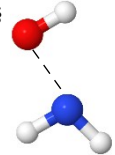
**Table S1** Characteristic structures on the  $S_1$  potential energy curve for the O–H dissociation in channel (1). The electronic states and the CI coefficients were

Structures	$S_0$		$S_1$	
	Conf.	CI Coeff.	Conf.	CI Coeff.
E1-[1] 	$\Psi_0$	0.9789	$\Psi_9^{\bar{1}0}$	0.9715
	$\Psi_{8,8}^{11,\bar{1}1}$	0.0764	$\Psi_{9,8,8}^{\bar{1}0,11,\bar{1}1}$	0.0694
	$\Psi_0$	0.9730	$\Psi_9^{\bar{1}0}$	0.9659
	$\Psi_8^{\bar{1}0}$	0.0649	$\Psi_{9,8}^{10,\bar{1}0}$	0.0844
E1-[3] <sup>§</sup> 	$\Psi_0$	0.9294	$\Psi_9^{\bar{1}0}$	0.9463
	$\Psi_8^{\bar{1}0}$	0.2293	$\Psi_{9,8}^{10,\bar{1}0}$	0.2441
	$\Psi_{8,8}^{10,\bar{1}0}$	0.2191	-	-

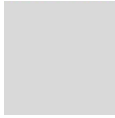
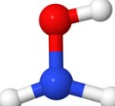
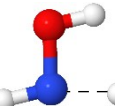
obtained from CASPT2(10,9) calculations.

E1-[2]<sup>†</sup>

**Table S2** Characteristic structures on the  $S_1$  potential energy curve for the N–O dissociation in channel (2). The electronic states and the CI coefficients were obtained from CASPT2(10,9) calculations.

Structures	S <sub>0</sub>		S <sub>1</sub>	
	Conf.	CI Coeff.	Conf.	CI Coeff.
E2-[1] 	$\Psi_0$	0.9518	$\Psi_9^{\bar{1}0}$	0.9453
	$\Psi_{8,8}^{\bar{1}0,10}$	0.1177	$\Psi_{9,8}^{10,\bar{1}1}$	0.1591
	-	-	$\Psi_{9,8,8}^{\bar{1}0,11,\bar{1}1}$	0.0939
E2-[2]* 	$\Psi_0$	0.9700	$\Psi_9^{\bar{1}0}$	0.9590
	$\Psi_{8,8}^{11,\bar{1}1}$	0.1348	$\Psi_{9,8,8}^{\bar{1}0,11,\bar{1}1}$	0.1202
E2-[3] <sup>§</sup> 	$\Psi_0$	0.8839	$\Psi_9^{\bar{1}0}$	0.9312
	$\Psi_8^{\bar{1}0}$	0.3061	$\Psi_{9,8}^{10,\bar{1}0}$	0.2852
	$\Psi_{8,8}^{10,\bar{1}0}$	0.2684	-	-

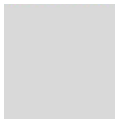
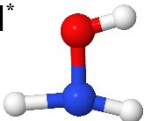
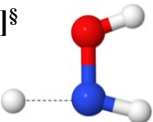
**Table S3** Characteristic structures on the S<sub>1</sub> potential energy curve for the N–H<sup>cis</sup> dissociation in channel (3). The electronic states and the CI coefficients were

Structures	S <sub>0</sub>		S <sub>1</sub>	
	Conf.	CI Coeff.	Conf.	CI Coeff.
E3-[1] 	$\Psi_0$	0.9807	$\Psi_9^{\bar{1}0}$	0.9733
	$\Psi_{8,8}^{11,\bar{1}1}$	0.0871	$\Psi_{9,8,8}^{\bar{1}0,11,\bar{1}1}$	0.0790
	$\Psi_0$	0.9740	$\Psi_9^{\bar{1}0}$	0.9669
	$\Psi_8^{\bar{1}0}$	0.0641	$\Psi_{9,8}^{10,\bar{1}0}$	0.0843
E3-[3] <sup>§</sup> 	$\Psi_0$	0.9438	$\Psi_9^{\bar{1}0}$	0.9483
	$\Psi_8^{\bar{1}0}$	0.1943	$\Psi_{9,8}^{10,\bar{1}0}$	0.2240
	$\Psi_{8,8}^{10,\bar{1}0}$	0.1637	-	-

obtained from CASPT2(10,9) calculations.

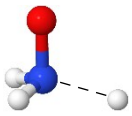
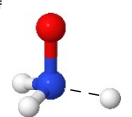
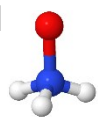
E3-[2]\*

**Table S4** Characteristic structures on the  $S_1$  potential energy curve for the N–H<sup>trans</sup> dissociation in channel (4). The electronic states and the CI coefficients were

Structures	$S_0$		$S_1$	
	Conf.	CI Coeff.	Conf.	CI Coeff.
E4-[1] 	$\Psi_0$	0.9790	$\Psi_{\bar{9}}^{\bar{1}0}$	0.9716
	$\Psi_{\bar{8},\bar{8}}^{11,\bar{1}1}$	0.0764	$\Psi_{\bar{9},\bar{8}}^{10,\bar{1}0}$	0.0753
E4-[2]* 	$\Psi_0$	0.9670	$\Psi_{\bar{9}}^{\bar{1}0}$	0.9587
	$\Psi_{\bar{8},\bar{8}}^{11,\bar{1}1}$	0.1033	$\Psi_{\bar{9},\bar{8}}^{10,\bar{1}0}$	0.1317
	$\Psi_{\bar{8},\bar{8}}^{10,\bar{1}0}$	0.0871	-	-
E4-[3]§ 	$\Psi_{\bar{9}}^{\bar{1}0}$	0.9417	$\Psi_0$	0.9309
	$\Psi_{\bar{9},\bar{8}}^{10,\bar{1}0}$	0.2568	$\Psi_{\bar{8}}^{\bar{1}0}$	0.2330
	-	-	$\Psi_{\bar{8},\bar{8}}^{10,\bar{1}0}$	0.1932

obtained from CASPT2(10,9) calculations.

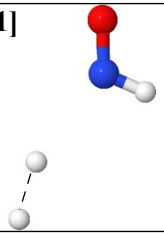
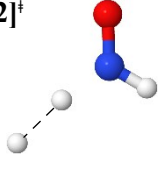
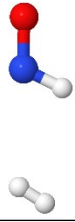
**Table S5** Characteristic structures on the  $S_1$  potential energy curve for the formation  $NH_3O$  in channel (5). The electronic states and the CI coefficients were

Structures	$S_0$		$S_1$	
	Conf.	CI Coeff.	Conf.	CI Coeff.
<b>E5-[1]</b> 	$\Psi_0$	0.6747	$\Psi_{\bar{9}}^{\bar{10}}$	0.9306
	$\Psi_{\bar{8}}^{\bar{10}}$	0.6018	$\Psi_{\bar{9},\bar{8}}^{10,\bar{10}}$	0.2924
	$\Psi_{\bar{8},\bar{8}}^{10,\bar{10}}$	0.3501	-	-
<b>E5-[2]<sup>†</sup></b> 	$\Psi_0$	0.9514	$\Psi_{\bar{9}}^{\bar{10}}$	0.9525
	$\Psi_{\bar{8}}^{\bar{11}}$	0.1352	$\Psi_{\bar{9},\bar{8}}^{10,\bar{11}}$	0.1129
	$\Psi_{\bar{8},\bar{8}}^{11,\bar{11}}$	0.0952	$\Psi_{\bar{9},\bar{8},\bar{8}}^{10,11,\bar{11}}$	0.1071
<b>E5-[3]</b> 	$\Psi_0$	0.9715	$\Psi_{\bar{9}}^{\bar{10}}$	0.9711
	$\Psi_{\bar{8},\bar{8}}^{11,\bar{11}}$	0.1018	$\Psi_{\bar{9},\bar{8},\bar{8}}^{10,11,\bar{11}}$	0.1180
	$\Psi_{\bar{8}}^{\bar{11}}$	0.0783	-	-

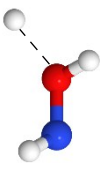
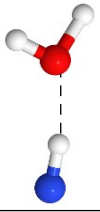

obtained from CASPT2(10,9) calculations.

**Table S6** Characteristic structures on the  $S_1$  potential energy curve for the formation of HNO and  $H_2$  in channel (6). The electronic states and the CI coefficients were obtained from CASPT2(10,9) calculations.



Structures	S <sub>0</sub>		S <sub>1</sub>	
	Conf.	CI Coeff.	Conf.	CI Coeff.
<b>E6-[1]</b> 	$\Psi_0$	0.9141	$\Psi_{\bar{9}}^{\bar{1}0}$	0.9086
	$\Psi_{\bar{8},\bar{8}}^{10,\bar{1}0}$	0.2000	$\Psi_{\bar{9},\bar{9}}^{10,\bar{1}1}$	0.2675
<b>E6-[2]<sup>‡</sup></b> 	$\Psi_0$	0.9212	$\Psi_{\bar{9}}^{\bar{1}0}$	0.9270
	$\Psi_{\bar{7}}^{\bar{1}0}$	0.0628	$\Psi_{\bar{9},\bar{8},\bar{8}}^{\bar{1}0,\bar{1}1,\bar{1}1}$	0.2569
<b>E6-[3]</b> 	$\Psi_0$	0.9493	$\Psi_{\bar{9}}^{\bar{1}0}$	0.9557
	$\Psi_{\bar{8},\bar{8}}^{10,\bar{1}0}$	0.1960	$\Psi_{\bar{9},\bar{8}}^{10,\bar{1}0}$	0.0772
	$\Psi_{\bar{8}}^{\bar{1}0}$	0.0743	-	-

**Table S7** Characteristic structures on the S<sub>1</sub> potential energy curve for the formation of NH-H<sub>2</sub>O complex. The electronic states and the CI coefficients were obtained from CASPT2(10,9) calculations.

Structures	$S_0$		$S_1$	
	Conf.	CI Coeff.	Conf.	CI Coeff.
<b>E7-[1]</b> 	$\Psi_{\bar{9}}^{\bar{1}0}$ $\Psi_{\bar{9},\bar{8}}^{10,\bar{1}0}$ -	0.9310 0.2992 -	$\Psi_0$ $\Psi_{\bar{8}}^{\bar{1}0}$ $\Psi_{\bar{8},\bar{8}}^{10,\bar{1}0}$	0.6965 0.5798 0.3567
<b>E7-[2]<sup>§</sup></b> 	$\Psi_0$ $\Psi_{\bar{8},\bar{8}}^{\bar{1}1,11}$	0.6858 0.1057	$\Psi_{\bar{9}}^{\bar{1}0}$ $\Psi_{\bar{9},\bar{8},\bar{8}}^{\bar{1}0,11,\bar{1}1}$	0.9706 0.1496
<b>G7-[3]</b> 	$\Psi_0$ $\Psi_{\bar{8},\bar{8}}^{\bar{1}1,11}$	0.6956 0.0510	$\Psi_{\bar{9}}^{\bar{1}0}$ $\Psi_{\bar{9},\bar{8},\bar{8}}^{\bar{1}0,11,\bar{1}1}$	0.9790 0.0718

**Table S8** Rate constants (k), enthalpies of activation ( $\Delta H^\ddagger$ ) and Gibbs free energy barriers ( $\Delta G^\ddagger$ ) for the formation of the precursors in the direct covalent bond dissociations in the  $S_0$  state, obtained based on transition state theory and the potential energy curves. Energies, rate constants and temperatures are in  $\text{kJ mol}^{-1}$ ,  $\text{s}^{-1}$  and K, respectively.

	$\Delta E^\ddagger$	$\Delta H^\ddagger$	$T_c$	T	$k^{\text{Class}}$	$k^{\text{Q-vib}}$	$k^{\text{S-Wig}}$	$\Delta G^\ddagger$
				308	$1.07 \times 10^{-22}$	$1.42 \times 10^{-21}$	$4.81 \times 10^{-21}$	199
<b>G1-[1] → G1-[2]<sup>‡</sup></b>	209	199	371	585	$4.00 \times 10^{-6}$	$1.38 \times 10^{-5}$	$2.29 \times 10^{-5}$	201
				1200	$1.18 \times 10^4$	$1.82 \times 10^4$	$2.11 \times 10^4$	210
				308	$3.42 \times 10^{-19}$	$8.42 \times 10^{-20}$	$1.81 \times 10^{-19}$	188
<b>G1-[1] → G2-[2]<sup>‡</sup></b>	216	190	257	585	$2.53 \times 10^{-5}$	$1.38 \times 10^{-4}$	$1.82 \times 10^{-4}$	190
				1200	$4.46 \times 10^4$	$7.75 \times 10^4$	$8.34 \times 10^4$	195
				308	$3.72 \times 10^{-24}$	$4.75 \times 10^{-23}$	$9.21 \times 10^{-23}$	207
<b>G1-[1] → G3-[2]<sup>‡</sup></b>	222	208	232	585	$7.49 \times 10^{-7}$	$2.39 \times 10^{-6}$	$3.01 \times 10^{-6}$	209
				1200	$5.79 \times 10^3$	$8.54 \times 10^3$	$9.07 \times 10^3$	217
				308	$1.37 \times 10^{-37}$	$3.00 \times 10^{-35}$	$8.02 \times 10^{-35}$	279
<b>G1-[1] → G4-[2]<sup>‡</sup></b>	314	281	310	585	$9.87 \times 10^{-14}$	$9.87 \times 10^{-13}$	$1.44 \times 10^{-12}$	281
				1200	$4.24 \times 10^0$	$8.82 \times 10^0$	$9.80 \times 10^0$	286

$\Delta E^\ddagger$  = energy barrier with respect to structure **G1-[1]**;  $T_c$  = crossover temperature;  $^\ddagger$  = transition structure;  $k^{\text{Class}}$  = rate constant obtained from classical transition state theory (TST);  $k^{\text{Q-vib}}$  = rate constant obtained with quantized vibrations including the zero-point vibrational energy;  $k^{\text{S-Wig}}$  = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order;  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  = enthalpy of activation and Gibbs free energy barrier with respect to structure **G1-[1]**.

**Table S9** Enthalpies ( $\Delta H^{\text{Rel}}$ ) and relative Gibbs free energies ( $\Delta G^{\text{Rel}}$ ) for direct covalent bond dissociations in the  $S_1$  state, obtained based on the transition state theory and barrierless potential energy curves ( $\Delta E^\ddagger = 0 \text{ kJ mol}^{-1}$ ). Energies and temperatures are in  $\text{kJ mol}^{-1}$  and K, respectively.

	$\Delta E^{\text{Rel}}$	$\Delta H^{\text{Rel}}$	T	$\Delta G^{\text{Rel}}$
			308	-10
<b>E1-[1]* <math>\rightarrow</math> E1-[3]§</b>	-227	-3	585	-15
			1200	-30
			308	-127
<b>E2-[2]* <math>\rightarrow</math> E2-[3]§</b>	-168	-124	585	-130
			1200	-136
			308	-12
<b>E3-[2]* <math>\rightarrow</math> E3-[3]§</b>	-12	-9	585	-28
			1200	-63

$\Delta E^{\text{Rel}}$  = relative energy with respect to the vertically excited structure; \* = vertically excited structure; § = structure at the intersection of the  $S_0$  and  $S_1$  potential energy curves;  $\Delta H^{\text{Rel}}$  and  $\Delta G^{\text{Rel}}$  = enthalpy and relative Gibbs free energy with respect to the vertically excited structure.

**Table S10** Enthalpies ( $\Delta H^{\text{Rel}}$ ) and relative Gibbs free energies ( $\Delta G^{\text{Rel}}$ ) for formations of  $\text{NH}_3\text{O}$ ,  $\text{HNO}$  and  $\text{H}_2$ , and the N-H.. $\text{H}_2\text{O}$  complex obtained from unimolecular isomerizations of dissociated structures in the  $S_0$  state,

computed based on transition state theory and barrierless potential energy curves ( $\Delta E^\ddagger = 0 \text{ kJ mol}^{-1}$ ). Energies and temperatures are in  $\text{kJ mol}^{-1}$  and K, respectively.

	$\Delta E^{\text{Rel}}$	$\Delta H^{\text{Rel}}$	T	$\Delta G^{\text{Rel}}$
			308	-215
<b>G5-[1]<sup>§</sup> → G5-[3]</b>	-241	-219	585	-212
			1200	-205
			308	-301
<b>G6-[1]<sup>§</sup> → G6-[3]</b>	-285	-279	585	-319
			1200	-363
			308	-154
<b>G7-[1] → G7-[3]</b>	-180	-154	585	-152
			1200	-152

$\Delta E^{\text{Rel}}$  = relative energy with respect to the precursor;  $^{\text{§}}$  = structure at the intersection of the  $S_0$  and  $S_1$  potential energy curves;  $\Delta H^{\text{Rel}}$  and  $\Delta G^{\text{Rel}}$  = enthalpy and relative Gibbs free energy with respect to dissociated structure.

**Table S11** Rate constants (k), enthalpies ( $\Delta H$ ) and Gibbs free energies ( $\Delta G$ ) for formations of  $\text{NH}_3\text{O}$ ,  $\text{HNO}$  and  $\text{H}_2$ , and the  $\text{N-H}\cdots\text{H}_2\text{O}$  complex from unimolecular isomerizations of dissociated structures in the  $S_1$  state, obtained based on the transition state theory and potential energy curves. Energies, rate constants and temperatures are in  $\text{kJ mol}^{-1}$ ,  $\text{s}^{-1}$  and K, respectively.

	$\Delta E^\ddagger$ (Rel)	$\Delta H^\ddagger$ (Rel)	$T_c$	<b>T</b>	$k^{\text{Class}}$	$k^{\text{Q-vib}}$	$k^{\text{S-Wig}}$	$\Delta G^\ddagger$ (Rel)
				308	$7.98 \times 10^2$	$2.40 \times 10^3$	$1.04 \times 10^4$	56
<b>E5-[1] → E5-[2]<sup>‡</sup></b>	55	52	437	585	$2.01 \times 10^7$	$3.14 \times 10^7$	$6.03 \times 10^7$	63
				1200	$6.56 \times 10^9$	$7.55 \times 10^9$	$9.20 \times 10^9$	81
				308				(-9)
<b>E5-[2]<sup>‡</sup> → E5-[3]</b>	(-41)	(-12)	-	585	-	Barrierless potential	-	(-7)
				1200				(-1)
				308	$6.38 \times 10^3$	$5.04 \times 10^5$	$1.42 \times 10^6$	42
<b>E6-[1]<sup>§</sup> → E6-[2]<sup>‡</sup></b>	71	57	324	585	$2.87 \times 10^9$	$1.49 \times 10^{10}$	$2.24 \times 10^{10}$	33
				1200	$4.88 \times 10^{12}$	$7.78 \times 10^{12}$	$8.71 \times 10^{12}$	12
				308				(-234)
<b>E6-[2]<sup>‡</sup> → E6-[3]</b>	(-221)	(-201)	-	585	-	Barrierless potential	-	(-262)
				1200				(-328)
				308				(-254)
<b>E7-[1] → E7-[3]<sup>§</sup></b>	(-249)	(-230)	-	585	-	Barrierless potential	-	(-272)
				1200				(-319)

$\Delta E^\ddagger$  and  $\Delta E^{\text{Rel}}$  = relative energies on the potential energy curve with respect to the precursor;  $T_c$  = crossover temperature; <sup>‡</sup> = transition structure; <sup>§</sup> = structure at the intersection of the  $S_0$  and  $S_1$  potential energy curves;  $k^{\text{Class}}$  = rate constant obtained from classical transition-state theory (TST);  $k^{\text{Q-vib}}$  = rate constant obtained with quantized vibrations including the zero-point vibrational energy;  $k^{\text{S-Wig}}$  = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order;  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  = enthalpy and Gibbs free energy barrier with respect to the precursor;  $\Delta H^{\text{Rel}}$  and  $\Delta G^{\text{Rel}}$  = enthalpy and relative Gibbs free energy with respect to the transition structure; (...) = value obtained based on barrierless potential.

**Table S12** Vertical excitation wavelengths ( $\lambda$ ) and energies ( $E^{\text{Ex}}$ ) and corresponding normalized oscillator strengths with respect to structure **G1-[1]**.

<b>Structure</b>	<b><math>\lambda</math> (nm)</b>	<b><math>E^{\text{Ex}}</math> (eV)</b>	<b>Oscillator strength</b>
<b>G1-[1]</b>	194	6.38	1.00
<b>G2-[2]<sup>†</sup></b>	435	2.85	0.007
<b>G3-[2]<sup>†</sup></b>	530	2.34	0.010
<b>G4-[2]<sup>†</sup></b>	646	1.92	0.010