Supporting Information

In-situ and real-time vibrational spectroscopic characterizations of the photodegradation of nitrite in the presence of methanediol

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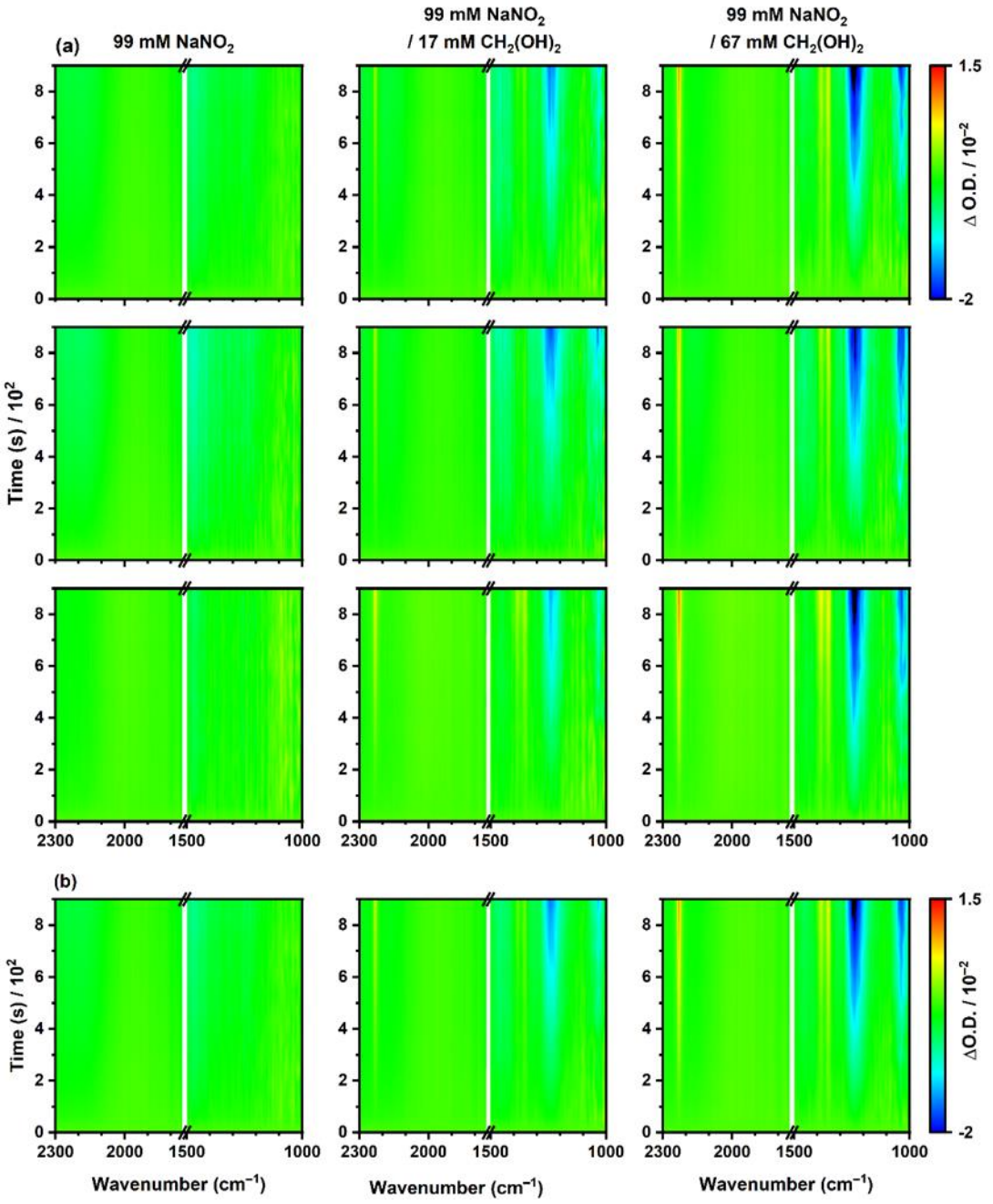


Figure S1. (a) Triplicate experiments of the time-evolved difference infrared spectra of 99 mM $NaNO_2$ aqueous solution in the presence of $CH_2(OH)_2$ at concentrations of 0, 17, and 67 mM upon continuous 365-nm photoexcitation (167 ± 9 mJ cm^{-2}). (b) The corresponding averaged spectra. The results of the mixture of 99 mM $NaNO_2$ and 67 mM $CH_2(OH)_2$ were replotted as (i) stack and (ii) contour plots in **Figure 4a**, respectively.

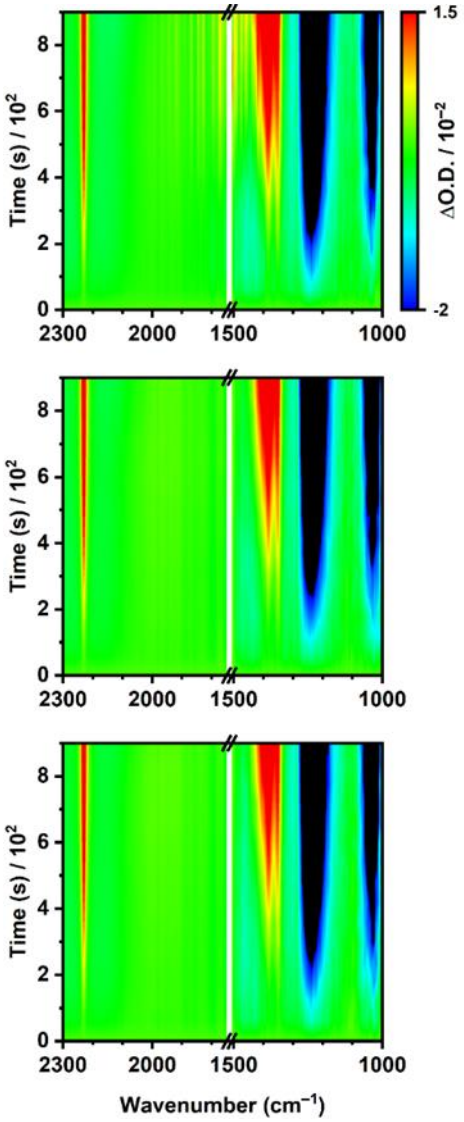


Figure S2. The contour plots of the triplicate results of the time-evolved difference infrared spectra upon continuous 365-nm photoexcitation (473 ± 3 mJ cm^{-2}) of the aqueous mixtures of 99 mM $NaNO_2$ and 67 mM $CH_2(OH)_2$.

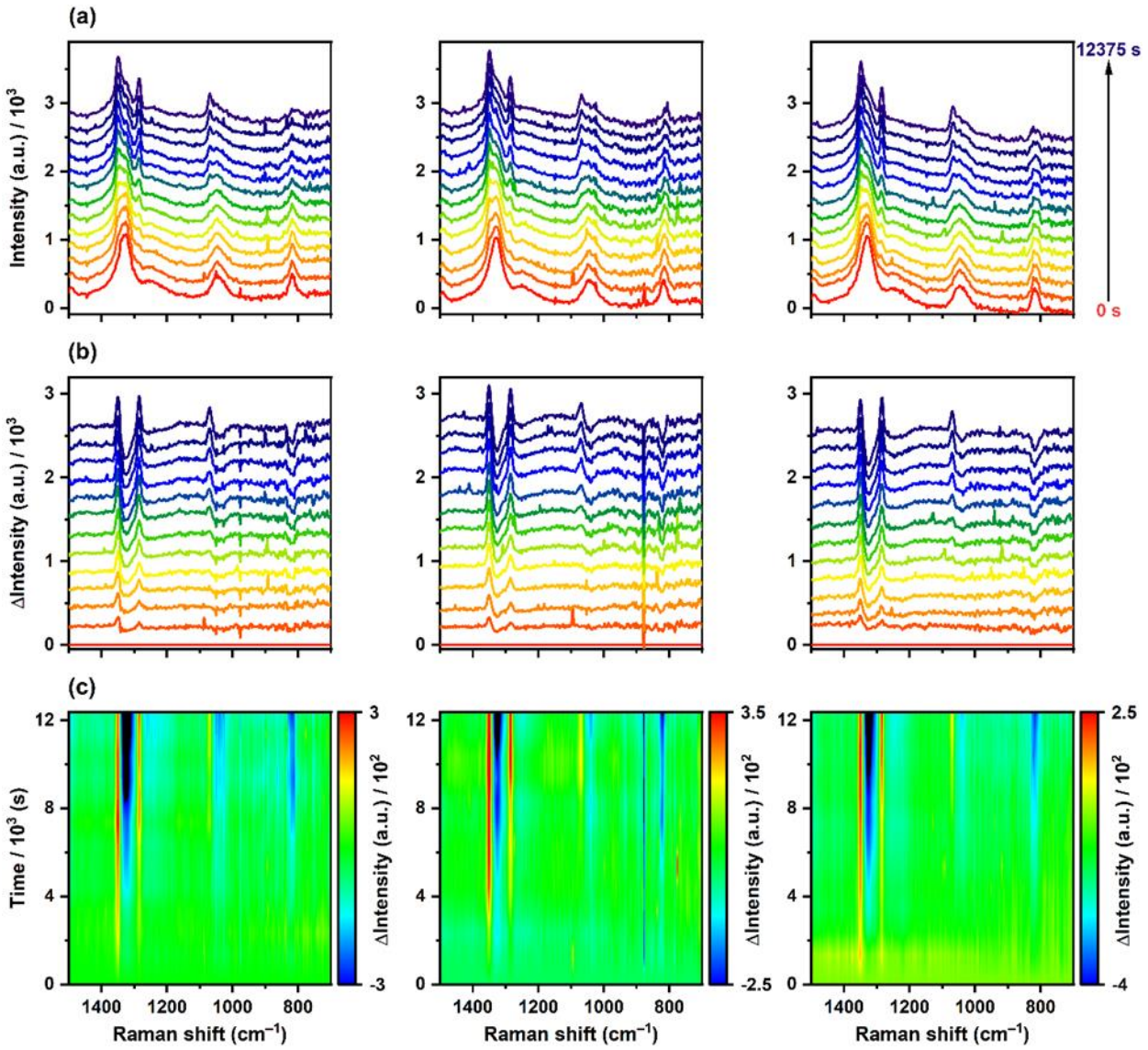


Figure S3. (a) Triplicate experiments of the time-evolved Raman spectra of the mixture containing 99 mM of $NaNO_2$ and 67 mM of $CH_2(OH)_2$ upon continuous 365-nm photoexcitation at 195 ± 11 mJ cm^{-2}. The corresponding time-resolved difference Raman spectra with respect to the unphotolyzed samples shown as (b) stack plot and (c) contour plot. The averaged spectra on (b) and (c) are shown in frames i and ii of **Figure 4c**, respectively.

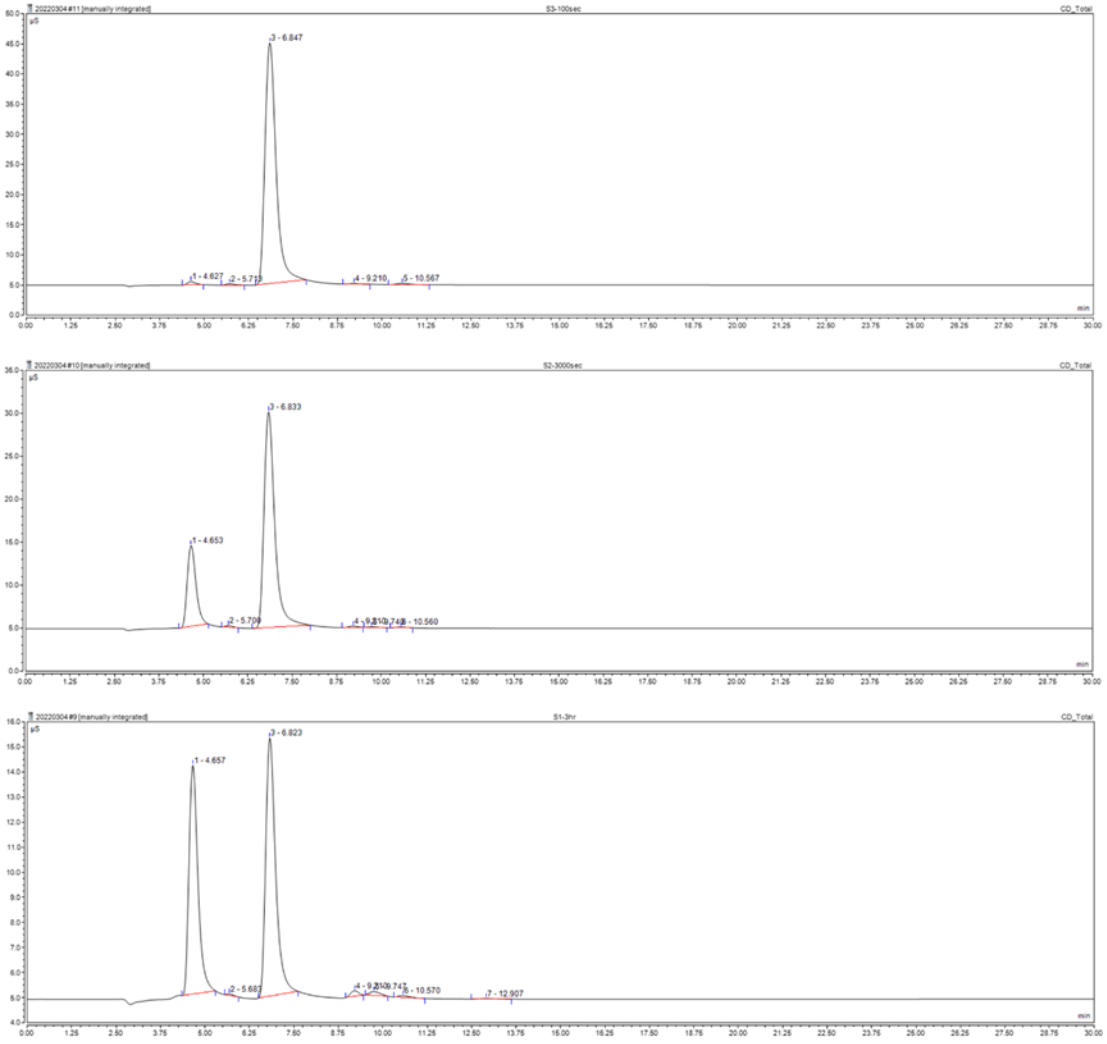


Figure S4. The original data of ion chromatographic plots for the mixture containing 99 mM $NaNO_2$ and 67 mM $CH_2(OH)_2$ upon 365-nm excitation (867 ± 13 mJ cm^{-2}) at different time slots: 100 s, 3000 s, and 10800 s. The thickened lines and scales of the frames are shown in **Figure 5**.

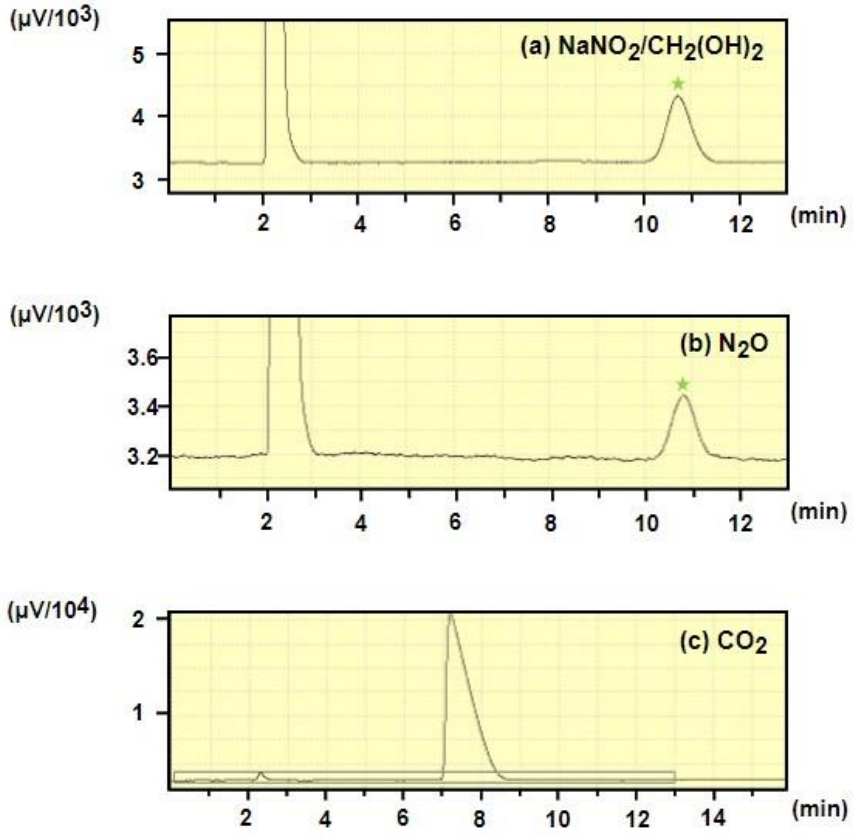
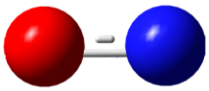
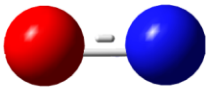
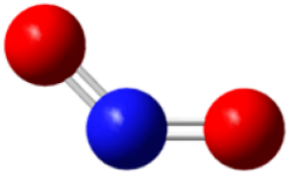
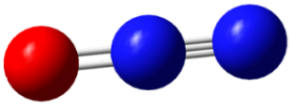
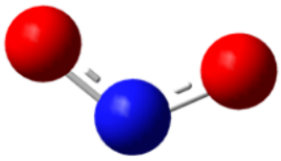
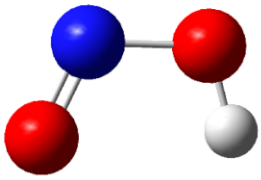
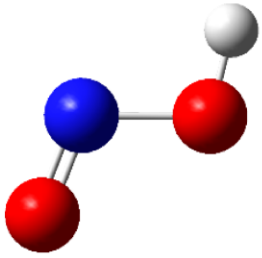
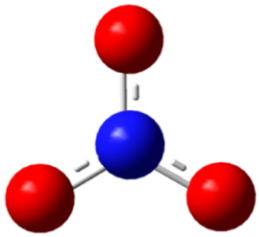
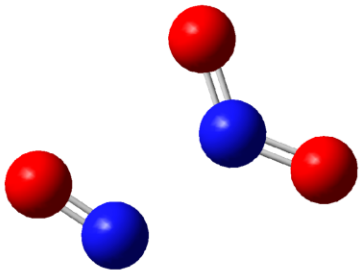
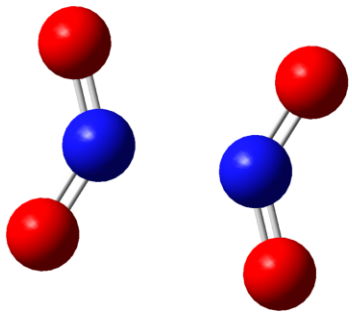
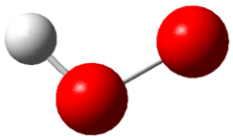
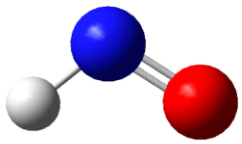
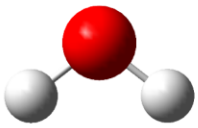


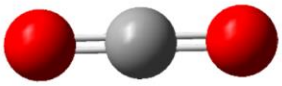
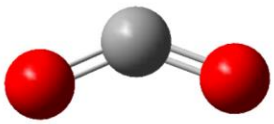
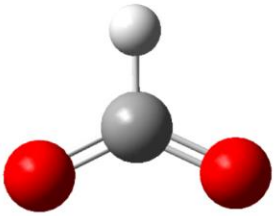
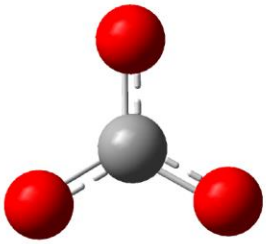
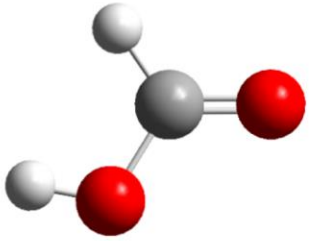
Figure S5. Chromatograms of (a) the vapor in the headspace of the mixture containing $NaNO_2$ / $CH_2(OH)_2$ = 98.9 mM / 66.7 mM upon 365-nm excitation for 3.5 hours, (b) 10 % N_2O diluted in N_2, and (c) pure CO_2 obtained from the gas chromatography.

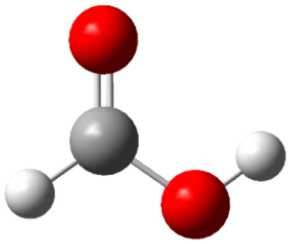
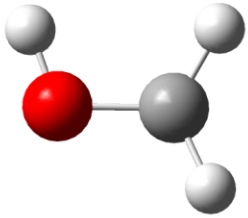
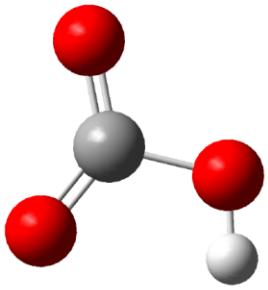
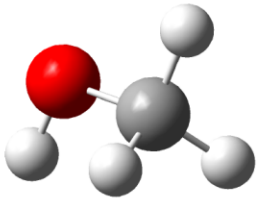
Table S1. The optimized molecular structures of relevant species in water using the B3LYP density functional theory method with basis sets of aug-cc-pVTZ and C-PCM to account for the solvent effect.

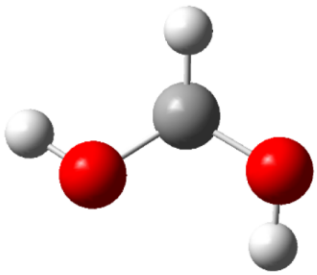
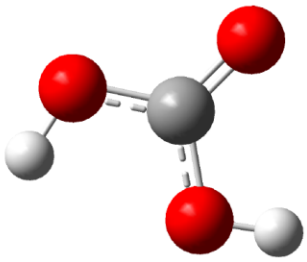
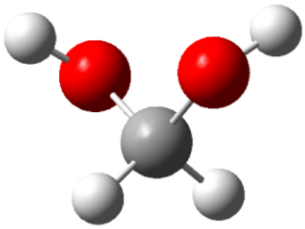
Molecule	Molecule Structure	Cartesian coordinate			
NO		Atom	X	Y	Z
		N	0.0000000	0.0000000	–0.6105960
		O	0.0000000	0.0000000	0.5342720
NO^-		Atom	X	Y	Z
		N	0.0000000	0.0000000	–0.6632440
		O	0.0000000	0.0000000	0.5803380
NO_2		Atom	X	Y	Z
		N	0.0000000	0.0000000	0.3208450
		O	0.0000000	1.0977090	–0.1403700
		O	0.0000000	–1.0977090	–0.1403700
N_2O		Atom	X	Y	Z
		N	0.0000000	0.0000000	–0.0741330
		N	0.0000000	0.0000000	–1.1937770
		O	0.0000000	0.0000000	1.1094210
NO_2^-		Atom	X	Y	Z
		N	0.0000000	0.0000000	0.4594880
		O	0.0000000	1.0661320	–0.2010260
		O	0.0000000	–1.0661320	–0.2010260

		Atom	X	Y	Z
c-HONO		N	0.0000000	0.5423420	0.0000000
		O	1.0864950	0.0845170	0.0000000
		O	–1.0129460	–0.3987760	0.0000000
		H	–0.5883930	–1.2823250	0.0000000
t-HONO		Atom	X	Y	Z
		N	–0.1673210	0.4848420	0.0000000
		O	–1.1007490	–0.2213050	0.0000000
		O	1.0319030	–0.2562360	0.0000000
		H	1.7220220	0.4264430	-0.0000010
NO_3^-		Atom	X	Y	Z
		N	0.0000000	0.0000000	0.0001960
		O	0.0000000	1.2557760	–0.0000570
		O	–1.0875340	–0.6278880	–0.0000570
		O	1.0875340	–0.6278880	–0.0000570
N_2O_3		Atom	X	Y	Z
		N	0.0000000	0.6431000	0.0000000
		O	1.2033870	0.6627810	0.0000000
		O	–0.7787640	1.5619780	0.0000000
		N	–0.6995770	–1.1205810	0.0000000
		O	0.1875060	–1.8069630	0.0000000

N_2O_4		Atom	X	Y	Z
		N	0.8958810	–0.0000520	0.0000170
		N	–0.8960370	0.0000200	–0.0000200
		O	1.3535260	1.0932590	0.0001230
		O	1.3537440	–1.0931350	–0.0001320
		O	–1.3535700	1.0931590	–0.0001220
		O	–1.3535650	–1.0932570	0.0001340
H^+		Atom	X	Y	Z
		H	0.0000000	0.0000000	0.0000000
HO_2		Atom	X	Y	Z
		O	0.0552890	–0.6077940	0.0000000
		H	–0.8846240	–0.8770750	0.0000000
		O	0.0552890	0.7174290	0.0000000
HNO		Atom	X	Y	Z
		N	0.0622290	0.5789260	0.0000000
		H	–0.9334410	0.9239620	0.0000000
		O	0.0622290	–0.6220550	0.0000000
H_2O		Atom	X	Y	Z
		O	0.0000000	0.0000000	0.1178240
		H	0.0000000	0.7619710	–0.4712970
		H	0.0000000	–0.7619710	–0.4712970

CO_2		Atom	X	Y	Z
		C	0.0000000	0.0000000	0.0000000
		O	0.0000000	0.0000000	1.1601680
		O	0.0000000	0.0000000	–1.1601680
CO_2^-		Atom	X	Y	Z
		C	0.0000000	0.0000000	0.3376020
		O	0.0000000	1.1426640	–0.1266010
		O	0.0000000	–1.1426640	–0.1266010
$HCOO^-$		Atom	X	Y	Z
		C	0.0000000	0.3318110	0.0000000
		H	–0.0012470	1.4503280	0.0000000
		O	1.1286870	–0.2142450	0.0000000
		O	–1.1285310	–0.2159050	0.0000000
CO_3^{2-}		Atom	X	Y	Z
		C	0.0000000	0.0000000	–0.0009160
		O	0.0000000	0.0000000	1.2978880
		O	0.0000000	1.1247580	–0.6486010
		O	0.0000000	–1.1247580	–0.6486010
c-HCOOH		Atom	X	Y	Z
		C	0.1251060	0.3682730	–0.0001010
		H	0.0360060	1.4626100	0.0000980
		O	1.1715200	–0.2208140	0.0000470
		O	–1.0469060	–0.2814390	–0.0000230
		H	–1.7835620	0.3457800	0.0003160

t-HCOOH		Atom	X	Y	Z
		C	0.0000000	0.4201010	0.0000000
		H	–0.3642030	1.4519880	0.0000000
		O	1.1615580	0.1033390	0.0000000
		O	–1.0297680	–0.4321000	0.0000000
		H	–0.6901170	–1.3425050	0.0000000
CH_2OH		Atom	X	Y	Z
		C	0.6853260	0.0272060	–0.0555160
		H	1.2406360	–0.8829180	0.1032800
		H	1.1098240	1.0016350	0.1359890
		O	–0.6700080	–0.1269080	0.0152240
		H	–1.1023480	0.7333100	–0.0279620
HCO_3^-		Atom	X	Y	Z
		C	0.0000000	0.1500050	0.0000000
		O	1.0216570	0.8588750	0.0000000
		O	–1.2073720	0.4741530	0.0000000
		O	0.2608750	–1.2368290	0.0000000
		H	–0.6012750	–1.6696190	0.0000000
CH_3OH		Atom	X	Y	Z
		C	0.0472790	0.6694150	0.0000000
		H	–0.8650990	–1.0655190	0.0000000
		H	–0.4423550	1.0721540	0.8897190
		H	–0.4423550	1.0721540	–0.8897190
		O	0.0472790	–0.7602240	0.0000000
		H	1.0878960	0.9865150	0.0000000

		Atom	X	Y	Z
$CH(OH)_2$		C	0.0017350	0.4993510	0.1576900
		H	0.0310340	1.4905500	–0.2877840
		O	1.0852590	–0.3205960	–0.0676670
		H	1.8946560	0.1594250	0.1449730
		O	–1.1834030	–0.1326710	–0.0714800
		H	–1.1509440	–1.0199420	0.3098490
		Atom	X	Y	Z
H_2CO_3		C	0.0000000	0.1361180	0.0000000
		O	0.9467940	–0.8159260	0.0000000
		O	0.2003580	1.3226130	0.0000000
		O	–1.2261470	–0.3905690	0.0000000
		H	–1.1829920	–1.3574730	0.0000000
		H	1.8149530	–0.3881740	0.0000000
		Atom	X	Y	Z
$CH_2(OH)_2$		C	0.0003000	0.5272420	0.0000020
		H	0.0177050	1.1497390	0.8944640
		H	–0.0175540	1.1495940	–0.8945070
		O	–1.1715480	–0.2526430	0.1044570
		H	–1.3146930	–0.7095590	–0.7326230
		O	1.1713170	–0.2527740	–0.1044380
		H	1.3145950	–0.7098890	0.7325020
O^-		Atom	X	Y	Z
		O	0.0000000	0.0000000	0.0000000

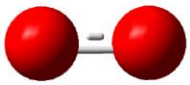
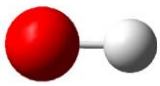
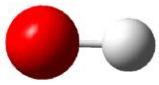
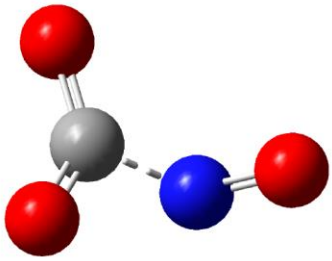
O_2		Atom	X	Y	Z
		O	0.0000000	0.0000000	0.6025320
		O	0.0000000	0.0000000	–0.6025320
OH		Atom	X	Y	Z
		O	0.0000000	0.0000000	0.1084880
		H	0.0000000	0.0000000	–0.8679000
OH^-		Atom	X	Y	Z
		O	0.0000000	0.0000000	0.1069920
		H	0.0000000	0.0000000	–0.8559380
$ONCO_2^-$		Atom	X	Y	Z
		C	0.5515770	–0.0000480	–0.0423990
		O	1.0217870	–1.1373780	0.0861030
		O	1.0223500	1.1370440	0.0863420
		N	–0.8652110	0.0004790	–0.5442660
		O	–1.7007600	–0.0000490	0.3355870

Table S2. The predicted Gibb's free energies of relevant species in water using the B3LYP density functional theory method with basis sets of aug-cc-pVTZ and C-PCM to account for the solvent effect. (Unit: Hartree)

Species	Sum of electronic and thermal Free Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Energies	Sum of electronic and zero-point Energies
NO	–129.959320	–129.936032	–129.936976	–129.939337
NO^-	–130.033914	–130.011117	–130.012062	–130.014428
NO_2	–205.176501	–205.149278	–205.150222	–205.153154
N_2O	–184.750318	–184.725403	–184.726347	–184.729023
NO_2^-	–205.359797	–205.332917	–205.333861	–205.336795
c-HONO	–205.798955	–205.770856	–205.771800	–205.774977
t-HONO	–205.800636	–205.772484	–205.773428	–205.776655
NO_3^-	–280.589763	–280.561204	–280.562148	–280.565313
N_2O_3	–335.135779	–335.101632	–335.102576	–335.107578
N_2O_4	–410.353447	–410.317887	–410.318831	–410.324138
H^+	–0.174563	–0.162203	–0.163147	–0.164564
HO_2	–150.987291	–150.961316	–150.962260	–150.965118
HNO	–130.538739	–130.513703	–130.514647	–130.517486
H_2O	–76.469244	–76.447816	–76.448761	–76.451596
CO_2	–188.675068	–188.650807	–188.651751	–188.654375
CO_2^-	–188.761979	–188.734761	–188.735705	–188.738661
$HCOO^-$	–189.395611	–189.367877	–189.368822	–189.371801
CO_3^{2-}	–264.181723	–264.152686	–264.153630	–264.156828
c-HCOOH	–189.841212	–189.812983	–189.813927	–189.817145
t-HCOOH	–189.842929	–189.814720	–189.815664	–189.818847

CH_2OH	–115.105161	–115.077817	–115.078761	–115.082152
HCO_3^-	–264.675631	–264.645403	–264.646347	–264.649873
CH_3OH	–115.753655	–115.726527	–115.727472	–115.730849
$CH(OH)_2$	–190.365566	–190.335058	–190.336002	–190.340023
H_2CO_3	–265.117312	–265.086682	–265.087626	–265.091392
$CH_2(OH)_2$	–191.013510	–190.983652	–190.984597	–190.988513
O^-	–75.295983	–75.279053	–75.279997	–75.281413
O_2	–150.400984	–150.377712	–150.378656	–150.381019
OH	–75.781604	–75.761370	–75.762314	–75.764675
OH^-	–75.971629	–75.952076	–75.953020	–75.955380
$ONCO_2^-$	–318.752138	–318.718765	–318.719709	–318.724338

Table S3. The predicted Gibb's free energy changes of the relevant reactions in water using the B3LYP density functional theory method with basis sets of aug-cc-pVTZ and C-PCM to account for the solvent effect.

Reaction	ΔG Hartree	ΔG kcal mol^{-1}	Reaction	ΔG Hartree	ΔG kcal mol^{-1}
$NO_2^- + OH \rightarrow NO_2 + OH^-$	–0.006729	–4.22	$CH(OH)_2 + NO \rightarrow t\text{-}HCOOH + HNO$	–0.056782	–35.63
$NO_2 + NO \rightarrow N_2O_3$	0.000042	0.03	$CH(OH)_2 + CH(OH)_2 \rightarrow CH_2(OH)_2 + c\text{-}HCOOH$	–0.123590	–77.53
$NO_2 + NO_2 \rightarrow N_2O_4$	–0.000445	–0.28	$CH(OH)_2 + CH(OH)_2 \rightarrow CH_2(OH)_2 + t\text{-}HCOOH$	–0.125307.	–78.60
$NO + OH \rightarrow c\text{-}HONO$	–0.058031	–36.42	$HCOO^- + OH \rightarrow CO_2^- + H_2O$	–0.054008	–33.89
$NO + OH \rightarrow t\text{-}HONO$	–0.059712	–37.47	$NO + CO_2^- \rightarrow ONCO_2^-$	–0.030839	–19.35
$CH_2(OH)_2 + OH \rightarrow CH(OH)_2 + H_2O$	–0.039696	–24.91	$ONCO_2^- \rightarrow NO + CO_2^-$	0.030839	19.35
$CH(OH)_2 + OH \rightarrow c\text{-}HCOOH + H_2O$	–0.163286	–102.46	$ONCO_2^- \rightarrow NO^- + CO_2$	0.043156	27.08
$CH(OH)_2 + OH \rightarrow t\text{-}HCOOH + H_2O$	–0.165003	–103.54	$NO^- + H_2O \rightarrow HNO$	–0.007210	–4.52
$CH(OH)_2 + NO \rightarrow c\text{-}HCOOH + HNO$	–0.055065	–34.55	$HNO + HNO \rightarrow N_2O + H_2O$	–0.142084	–89.16