Electronic Supplementary Information

Reaction of H + HONO in solid *para*-hydrogen: infrared spectrum of •ONH(OH)

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Tables and Figures in the ESI

Comparison of vibrational wavenumbers (cm^{-1}) of *trans*- and *cis*-HONO in various matrices and in the gaseous phase is presented in Table S1. Comparison of vibrational wavenumbers (cm^{-1}) of *trans*- and *cis*-DONO and *trans*- and *cis*-$HO^{15}NO$ in solid *p*-H_2 is presented in Table S2. Harmonic wavenumbers (cm^{-1}) of $HN(OH)_2$, HN(OH)OD, and $H•^{15}N(OH)_2$, and isotopic ratios D/H and $^{15}N/^{14}N$ of $HN(OH)_2$ calculated with the B3LYP/aug-cc-pVTZ method are presented in Table S3; those of $•N(OH)_2$ and $HN(OH)_2$ are presented in Tables S4 and S5, respectively. Harmonic wavenumbers (cm^{-1}) of •ONH(OH), •ONH(OD), and $•O^{15}NH(OH)$, and isotopic ratios D/H and $^{15}N/^{14}N$ of •ONH(OH) calculated with the B3LYP/aug-cc-pVTZ method are presented in Table S4; those of $•N(OH)_2$ are presented in Tables S4 and S5, respectively.

Spectra in the ν_3 region of H_2O recorded at various stages of an experiment is presented in Fig. S1. Partial spectra of a HONO/NH_3/Cl_2/*p*-H_2 matrix recorded at various stages of an experiment are presented in Fig. S2; those of matrices DONO/NH_3/*p*-H_2 and $HO^{15}NO$/NH_3/*p*-H_2 are presented in Figs. S3 and S4, respectively. Geometries of a less stable conformer of. $•N(OH)_2$ optimized with the B3LYP/aug-cc-pVTZ methodis shown in Fig. S5.

Table S1 Comparison of vibrational wavenumbers (cm^{-1}) of *trans*- and *cis*-HONO in various matrices and in the gaseous phase.

mode	*trans*-HONO					*cis*-HONO				
	p-H_2	Ar	Kr	N_2	gas	*p*-H_2	Ar	Kr	N_2	gas
ν_1	3574.5	3572.6 /3568.5	3551.1	3558.0	3590.7	3417.7	3412.4 /3410.7	3399.7	3410.0	3426.0
ν_2	1692.0	1689.1 /1688.0	1684.0	1684.0	1689.0	1635.8	1634.0 /1632.8	1629.0	1633.0	1640.5
ν_3	1264.9	1265.8 /1263.9	1265.3	1298.0	1266.0	-	-	1315.2	-	1302.0
ν_4	792.7	800.4 /796.6	794.5	815.0	800.0	850.2	853.1 /850.2	851.9	865.0	851.9
ν_5	609.5	608.7	606.7	625.0	609.0	606.2	608.0	616.6	-	609.0
ν_6	551.8	549.4	549.1	583.0	549.4	641.8	638.4	635.0	658.0	639.8
ref.	this work	[a]	[b]	[c]	[d]	this work	[a]	[b]	[c]	[d]

[a] I. Kleiner, J. Guilmot, M. Carleer and M. Herman, *J. Mol. Spectrosc.*, 1991, **149**, 341 – 347.
[b] Z. Mielke, K. G. Tokhadze, Z. Latajka and E. Ratajczak, *J. Phys. Chem.*, 1996, **100**, 539–545.
[c] R. T. Hall and G. C. Pimentel, *J. Chem. Phys.*, 1963, **38**, 1889–1897.
[d] L. Khriachtchev, J. Lundell, E. Isoniemi and M. Rasanen, *J. Chem. Phys.*, 2000, **113**, 4265–4273.

Table S2 Comparison of vibrational wavenumbers (cm^{-1}) of *trans*- and *cis*-DONO and *trans*- and *cis*-$HO^{15}NO$ in solid *p*-H_2.

mode	*trans*-DONO	*cis*-DONO	*trans*-$HO^{15}NO$	*cis*-$HO^{15}NO$
ν_1	2638.9	2527.3	3574.5	3417.1
ν_2	1686.0	1621.8	1662.2	1607.8
ν_3	1013.4	-	1264.7	-
ν_4	741.4	811.3	776.5	~833
ν_5	592.5	593.0	598.4	595.0
ν_6	508.6	-	552.3	-

Table S3 Harmonic wavenumbers (cm^{-1}) of $HN(OH)_2$, HN(OH)OD, and $H•{}^{15}N(OH)_2$, and isotopic ratios D/H and $^{15}N/^{14}N$ of $HN(OH)_2$ calculated with the B3LYP/aug-cc-pVTZ method.

mode	$HN(OH)_2$	HN(OH)OD	$H^{15}N(OH)_2$	D/H	$^{15}N/^{14}N$	PED (%)[a]
ν_1	3790 (56)	3789 (46)	3790 (56)	1.000	1.000	νO1-H2 (50) + νO2-H3 (50)
ν_2	3789 (35)	2761 (26)	3789 (36)	0.729	1.000	νO1-H2 (50) + νO2-H3 (50)
ν_3	3482 (6)	3482 (7)	3474 (6)	1.000	0.998	νN-H1 (100)
ν_4	1539 (0)	1530 (2)	1539 (0)	0.994	1.000	δH1-N-O4 (83)
ν_5	1466 (5)	1409 (23)	1460 (6)	0.961	0.996	δH2-O1-N (36) + δH3-O2-N (36) + γN-O2-O1-H1 (26)
ν_6	1310 (80)	1195 (78)	1308 (84)	0.912	0.999	δH2-O1-N (41) + δH3-O2-N (41) + δH1-N-O_2 (16)
ν_7	1145 (106)	993 (47)	1143 (105)	0.867	0.999	γN-O2-O1-H1 (49) + δH2-O1-N (13) + δH3-O2-N (13)
ν_8	930 (2)	909 (6)	913 (2)	0.977	0.981	νO1-N (38) + νO2-N (38) + γN-O2-O1-H1 (14) + δO1-N-O_2 (10)
ν_9	861 (201)	859 (203)	844 (192)	0.998	0.981	νO1-N (49) + νO2-N (49)
ν_{10}	530 (1)	528 (3)	527.4 (1)	0.997	0.995	δO1-N-O_2 (86)
ν_{11}	440 (127)	400 (96)	439.2 (127)	0.908	0.998	τH2-O1-N-O_2 (50) + τH1-O2-N-O1 (50)
ν_{12}	305 (35)	250 (24)	304.9 (35)	0.820	1.000	τH2-O1-N-O_2 (49) + τH1-O2-N-O1 (49)

[a] Calculated by VEDA 4f software. Vibrations with contribution >10% are included; the coefficients are listed in parentheses.

[b] Mode description: ν: stretch; δ: bend; γ: out-of-plane deformation ; τ: torsion.

[c] Calculated IR intensities in km mol^{-1} are given in parenthesis.

Table S4 Harmonic wavenumbers (cm^{-1}) of •ONH(OH), •ONH(OD), and •O^{15}NH(OH), and isotopic ratios D/H and $^{15}N/^{14}N$ of •ONH(OH) calculated with the B3LYP/aug-cc-pVTZ method.

mode	•ONH(OH)	•ONH(OD)	•O^{15}NH(OH)	D/H	$^{15}N/^{14}N$
ν_1	3729.4 (67)[a]	2714.2 (38)[a]	3729.4 (68)[a]	0.728	1.000
ν_2	3369.3 (3)	3369.6 (4)	3361.6 (3)	1.000	0.998
ν_3	1506.7 (55)	1443.6 (31)	1494.1 (41)	0.958	0.992
ν_4	1411.6 (66)	1411.0 (74)	1403.2 (78)	1.000	0.994
ν_5	1285.9 (6)	1080.0 (17)	1276.4 (7)	0.840	0.993
ν_6	942.0 (188)	899.6 (162)	931.3 (179)	0.955	0.989
ν_7	761.7 (123)	759.6 (114)	751.7 (123)	0.997	0.987
ν_8	544.0 (13)	510.4 (16)	540.8 (13)	0.938	0.994
ν_9	239.6 (126)	185.7 (81)	239.1 (126)	0.775	0.998

[a] Calculated IR intensities in km mol^{-1} are given in parenthesis.

Table S5 Harmonic wavenumbers (cm^{-1}) of $•N(OH)_2$, •N(OH)OD, and $•^{15}N(OH)_2$, and isotopic ratios D/H and $^{15}N/^{14}N$ of $•N(OH)_2$ calculated with the B3LYP/aug-cc-pVTZ method.

mode	$•N(OH)_2$	•N(OH)OD	$•^{15}N(OH)_2$	D/H	$^{15}N/^{14}N$
ν_1	3779.0 (101)[a]	3660.1 (40)[a]	3779.0 (101)[a]	0.969	1.000
ν_2	3659.9 (38)	2751.6 (56)	3659.9 (38)	0.752	1.000
ν_3	1436.7 (65)	1412.6 (58)	1426.9 (70)	0.983	0.993
ν_4	1323.1 (63)	1139.2	1320.6 (62)	0.861	0.998
ν_5	1040.5 (172)	976.4 (166)	1025.9 (156)	0.938	0.986
ν_6	960.6 (63)	906.1 (8)	944.8 (70)	0.943	0.984
ν_7	570.8 (23)	552.3 (25)	567.8 (22)	0.968	0.995
ν_8	343.7 (8)	299.6 (18)	342.7 (8)	0.872	0.997
ν_9	224.3 (221)	192.8 (154)	3779.0 (101)	0.969	1.000

[a] Calculated IR intensities in km mol^{-1} are given in parenthesis.

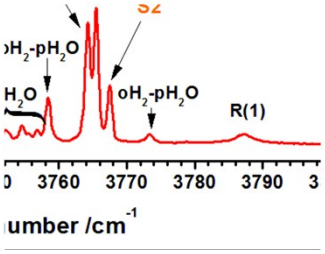

Fig. S1 Spectra in the ν_3 region of H_2O recorded at various stages of an experiment. (a) Spectra of a HONO/NH_3/p-H_2 matrix recorded after irradiation at 365 nm for 10 min. (b) Spectra of the same matrix recorded 6 h in darkness after irradiation. The assignments according to S. Tam and M. E. Fajadro (*Low Temp. Phys.,* 2000, **26**, 653-660) and K. A. Kufeld *et al*. (*J. Phys. Chem. Lett*., 2012, **3**, 342-347) are indicated. Lines marked S1 and S2 are satellite lines of R(0); see text. Red arrows indicate their changes in intensity.

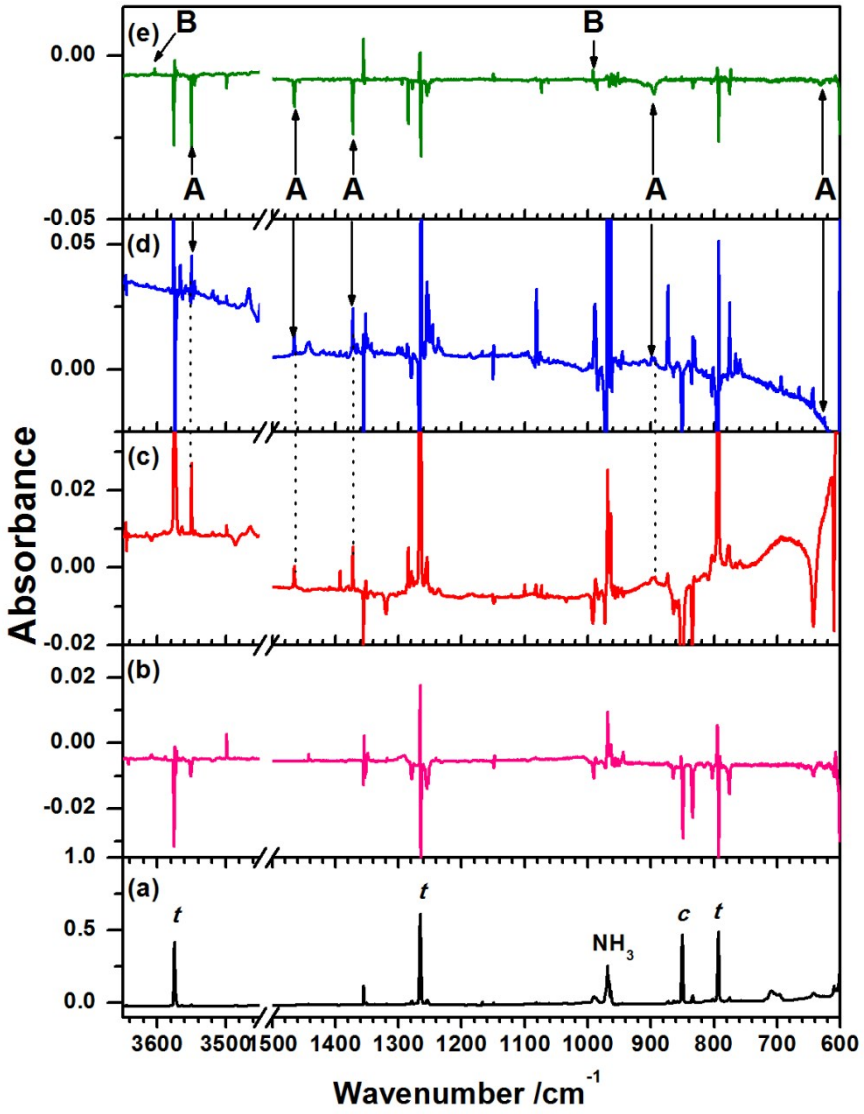

Fig. S2 Partial spectra of a HONO/NH_3/Cl_2/*p*-H_2 matrix recorded at various stages of an experiment. (a) Absorption spectrum after deposition at 3.3 K for 6 h. (b) Difference spectrum of this matrix upon irradiation with light at 405 nm for 30 min. (c) Difference spectrum of this matrix recorded after IR irradiation for 45 min; (d) Difference spectrum of this matrix recorded 4 h in darkness after irradiation; (e) Difference spectrum of this matrix upon secondary photolysis at 405 nm for 10 min. Lines in groups A [•ONH(OH)] and B [•$N(OH)_2$] are marked with arrow and labels; *t* and *c* indicate *trans*- and *cis*-HONO, respectively.

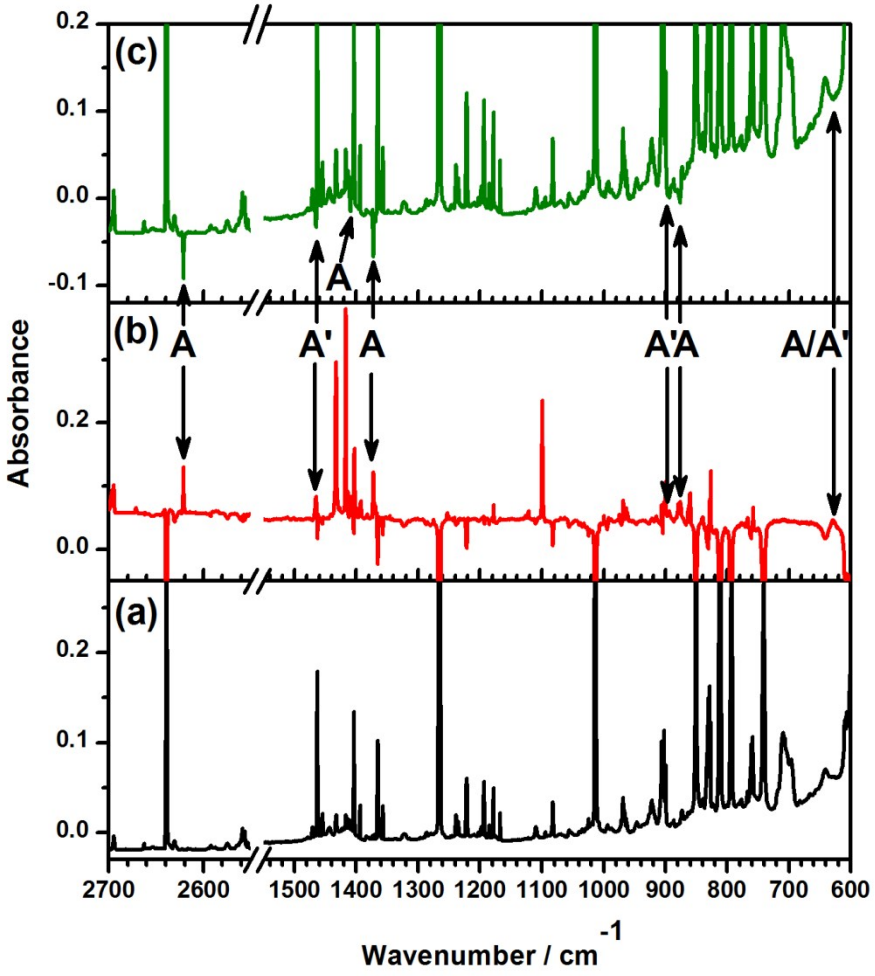

Fig. S3 Partial spectra of a DONO/NH_3/*p*-H_2 matrix recorded at various stages of an experiment. (a) Absorption spectrum after deposition at 3.3 K for 7.5 h. (b) Difference spectrum of this matrix upon irradiation with light at 365 nm for 15 min. recorded 3h after irradiation; (c) Difference spectrum of this matrix upon secondary photolysis at 405 nm for 10 min. Lines in groups A [•ONH(OD)] and A' [•ONH(OH)] are marked with arrow and labels.

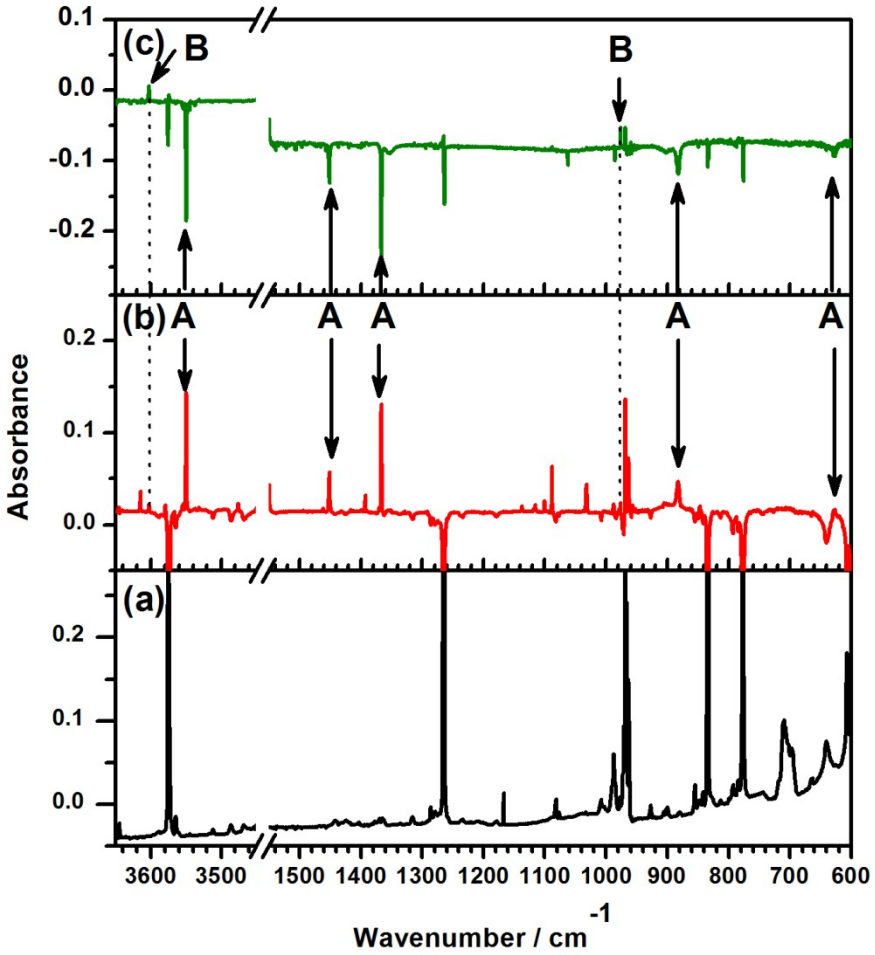

Fig. S4 Partial spectra of a $HO^{15}NO/NH_3/p\text{-}H_2$ matrix recorded at various stages of an experiment. (a) Absorption spectrum after deposition at 3.3 K for 8 h. (b) Difference spectrum of this matrix upon irradiation with light at 365 nm for 15 min. recorded 3h after irradiation; (c) Difference spectrum of this matrix upon secondary photolysis at 405 nm for 10 min. Lines in groups A [$\bullet O^{15}NH(OH)$] and B [$\bullet{}^{15}N(OH)_2$] are marked with arrow and labels.

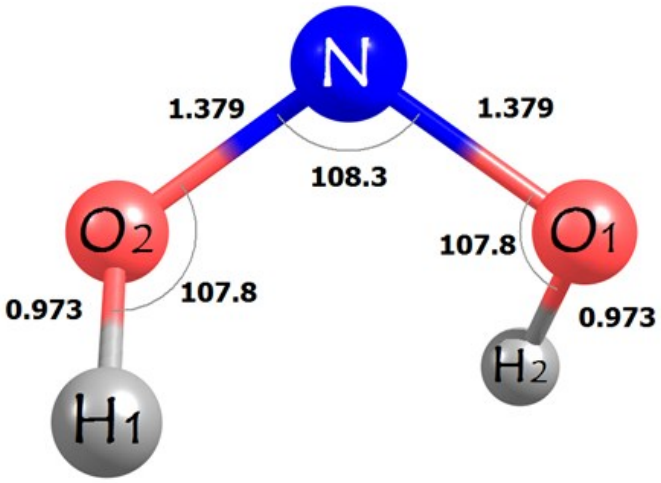

Fig. S5 Geometries of a less stable conformer of. •$N(OH)_2$. The structures were optimized with the B3LYP/aug-cc-pVTZ method; bond lengths are in Å and angles in degree.