

Supporting Information

Photo-induced reactions between glyoxal and hydroxylamine in cryogenic matrices

Barbara Golec,^{a*} Magdalena Saldyka^{b*} and Zofia Mielke^b

^a *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

^b *Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland*

Corresponding author:

dr Barbara Golec, e-mail: bgolec@ichf.edu.pl

dr Magdalena Saldyka, e-mail: magdalena.saldyka@chem.uni.wroc.pl

Table S1. The comparison of the observed wavenumbers (cm^{-1}) and wavenumber shifts ($\Delta\nu = \nu_{\text{GH}} - \nu_{\text{M}}$) for the **Gly-HA** (GH) complexes present in the Ar and N_2 matrices with the corresponding calculated values for the complexes **I_{GH}** and **II_{GH}**. In parentheses the calculated bands intensities are given (km mol^{-1}).

Approximate description	Experimental						Calculated	
	Ar			N_2			$\Delta\nu$	
	ν_{M}	ν_{GH}	$\Delta\nu^1$	ν_{M}	ν_{GH}^2	$\Delta\nu^1$	I_{GH}	II_{GH}
NH₂OH-CHOCHO								
<i>Hydroxylamine</i>								
$\nu(\text{OH})$	3635.5	3521.0 3512.4	-118.8	3637.6	3541.1 3520.9 3515.8	-96.5 -119.2	-145(7)	-106(383)
$\delta(\text{NOH})$	1351.2	1412.1 1410.2	+60.9	1367.4	1416.6 1399.7	+49.2 +32.3	+61(63)	+72(29)
$\omega(\text{NH}_2)$	1118.3	1129.0 1125.8	+9.1	1133.0	1142.6	+9.6	+14(11)	+24(112)
$\nu(\text{NO})$	895.6			895.3	898.8	+3.5	+14(3)	+9(8)
<i>Glyoxal</i>								
$\nu(\text{CH})$	2860.1 2854.9	2857.6	-0.4	2857.1	2875.6	+18.5	-9(60) +12(39)	+15(53) +20(1)
$\nu(\text{C=O})$	1724.5	1719.0	-5.5	1730.1	1720.2 1723.1	-9.9 -7.0	-4(122) +4(23)	-11(126) -6(20)
$\gamma(\text{CH})$	812.1 807.8			807.4	820.8	+13.4	+37(0)	+23(8)
ND₂OD-CHOCHO								
<i>Hydroxylamine</i>								
$\nu(\text{OD})$	2685.1	2604.0 2598.0	-84.1	2686.9	2619.2 2616.7	-68.9	-106(42)	-77(202)
$\delta(\text{NOD})$	1034.5	1068.0 1064.5	+33.5	1043.2			+38(6)	+38(7)
$\omega(\text{ND}_2)$	915.0			916.5	927.1	+10.6	+0(29)	+14(40)
$\nu(\text{NO})$	818.4			827.6	838.0 836.6	+9.7	+28(41)	+21(40)
<i>Glyoxal</i>								
$\nu(\text{CH})$	2860.1 2854.9			2857.1	2876.3	+19.2	+12(36) -10(59)	+20(1) +15(48)
$\nu(\text{C=O})$	1724.5	1719.6	-4.9	1730.1	1720.5	-9.6	+4(25) -5(125)	-6(20) -11(128)
$\delta(\text{CH})$	1313.6	1317.9	+4.3	1322.5			+1(1) +2(4)	+12(5) +11(9)
$\gamma(\text{CH})$	812.1 807.8			807.4	820.9	+13.5	+41(5)	+22(4)

¹ In the case when the splitting of the band was observed the average of the two wavenumbers at which the two peaks appeared was taken into account to calculate $\Delta\nu$ value. ² The wavenumbers in normal and italic letters are due to structure **I_{GH}** and **II_{GH}**, respectively.

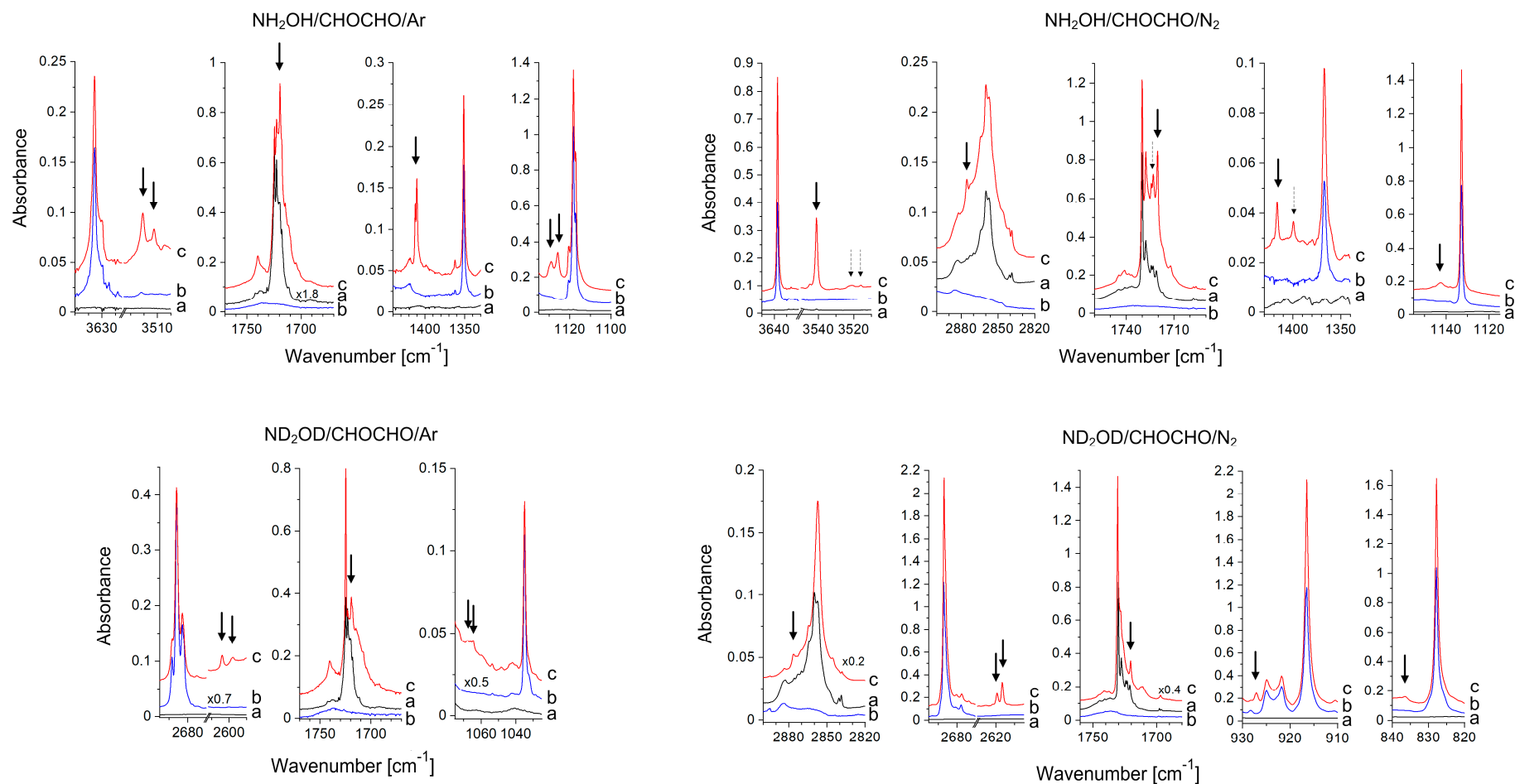


Figure S1. The spectra of the CHOCHO/Ar(N₂) (a), NH₂OH/Ar(N₂) (b) and CHOCHO/NH₂OH(NH₂OH)/Ar(N₂) (c) matrices recorded after matrix deposition at 11 K. The bands of Gly-HA complexes are indicated by the arrows. Dashed and solid arrows correspond to the I_{GH} and II_{GH} structures, respectively.

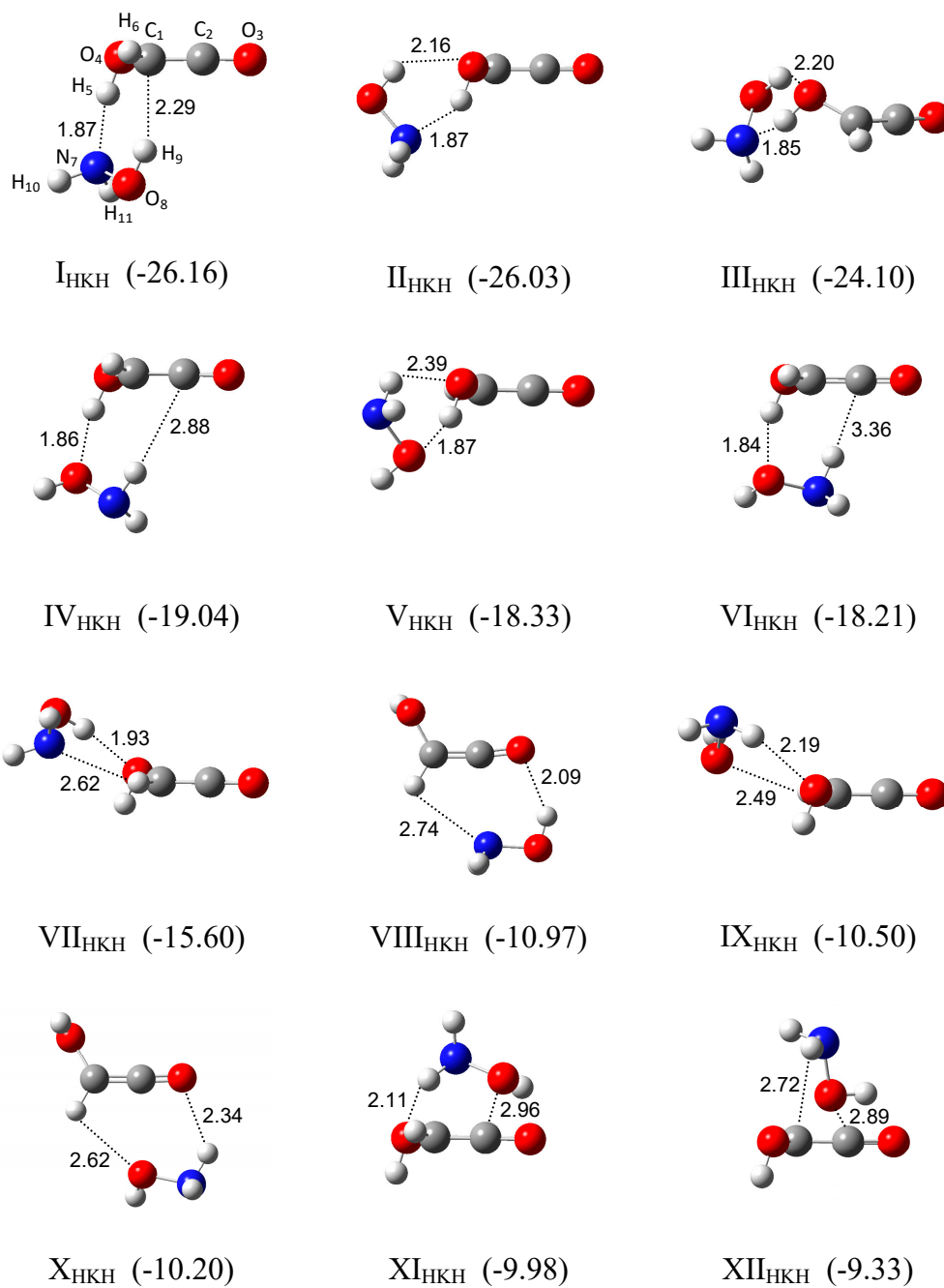


Figure S2. The MP2/6-311++G(2d,2p) optimized structures of the hydroxyketene-hydroxylamine, **I_{HKH}** - **XII_{HKH}**, complexes. The $\Delta E^{\text{CP}}(\text{ZPE})$ binding energies in kJ mol⁻¹ are given in parentheses. The intermolecular distances are given in Å.

Table S2. Selected geometrical parameters of the hydroxylamine and hydroxyketene subunits in their binary complexes (**I_{HKH}**-**VI_{HKH}**). For comparison the corresponding parameters of the monomers (**M**) are also given. The complexes are numbered in the same way as presented in Fig. S2. Bond distances are given in Å, angles in °.

<i>Parameter</i>	M	I_{HKH}	II_{HKH}	III_{HKH}	VI_{HKH}	V_{HKH}	VI_{HKH}
r C ₁ -C ₂	1.327	1.333	1.327	1.327	1.329	1.327	1.327
r C ₂ -O ₃	1.170	1.170	1.171	1.172	1.171	1.171	1.173
r C ₁ -O ₄	1.398	1.393	1.394	1.394	1.392	1.394	1.393
r C ₁ -H ₆	1.077	1.078	1.078	1.078	1.079	1.078	1.078
r O ₄ -H ₅	0.960	0.978	0.977	0.978	0.970	0.969	0.970
r O ₈ -H ₇	0.959	0.966	0.966	0.965	0.960	0.960	0.960
r O ₈ -N ₉	1.448	1.445	1.443	1.442	1.454	1.455	1.452
r N ₉ -H ₁₀	1.012	1.013	1.012	1.012	1.015	1.015	1.013
r N ₉ -H ₁₁	1.012	1.013	1.012	1.012	1.013	1.012	1.014
R H ₅ ...N ₉		1.874	1.871	1.853			
R C ₁ ...H ₇		2.295					
R H ₇ ...O ₄			2.155	2.198			
R H ₅ ...O ₈					1.865	1.873	1.842
R C ₁ ...H ₁₀					2.603		
R H ₁₀ ...O ₄						2.387	
R H ₁₁ ...O ₄							2.713
θ C ₂ -C ₁ -O ₃	179.2	178.7	179.1	179.3	179.2	179.2	179.5
θ C ₂ -C ₁ -O ₄	119.6	119.6	119.9	120.3	119.6	119.9	119.7
θ C ₂ -C ₁ -H ₆	119.0	117.8	118.5	118.6	118.2	118.6	118.7
θ H ₆ -C ₁ -O ₄	120.9	121.0	121.2	120.8	121.3	121.1	121.3
θ C ₁ -O ₄ -H ₅	107.8	106.3	108.1	107.8	106.8	108.5	107.0
θ H ₇ -O ₈ -N ₉	101.7	101.8	101.8	101.9	102.2	102.0	102.2
θ O ₈ -N ₉ -H ₁₀	103.6	104.3	104.4	104.4	103.4	103.5	103.2
θ O ₈ -N ₉ -H ₁₁	103.6	104.4	104.6	104.5	103.2	103.1	103.7
θ H ₁₀ -N ₉ -H ₁₁	105.8	106.2	106.4	106.5	106.1	105.8	105.9
θ C ₂ -C ₁ -H ₇		93.2					
θ O ₄ -H ₅ -N ₉		162.4	146.0	148.2			
θ H ₅ -N ₉ -O ₈		104.8	93.1	93.8			
θ H ₅ -N ₉ -H ₁₀		118.3	122.5	121.8			
θ H ₅ -N ₉ -H ₁₁		117.3	121.6	121.7			
θ O ₄ -H ₇ -O ₈			133.0	131.6			
θ O ₄ -H ₅ -O ₈					164.6	149.0	159.7
θ C ₂ -C ₁ -H ₁₀					88.1		
θ O ₄ -H ₁₀ -N ₉						123.9	
θ O ₄ -H ₁₁ -N ₉							115.4
φ O ₃ -C ₁ -C ₂ -O ₄	177.0	-123.2	-160.7	152.6	-161.6	-164.7	132.2
φ O ₃ -C ₁ -C ₂ -H ₆	-11.4	71.0	12.9	-21.0	30.0	8.5	-41.3
φ C ₂ -C ₁ -O ₄ -H ₅	103.6	103.7	-103.4	101.0	109.5	-102.4	106.9
φ H ₆ -C ₁ -O ₄ -H ₅	85.0	-90.9	83.3	-85.6	-81.4	84.6	-79.7
φ H ₇ -O ₈ -N ₉ -H ₁₀	-124.8	-125.4	-126.3	-124.5	-122.9	-123.5	-128.6
φ H ₇ -O ₈ -N ₉ -H ₁₁	124.8	123.4	122.2	123.9	126.7	126.4	121.1
φ O ₄ -H ₅ -N ₉ -O ₈		2.4	3.3	0.0			
φ C ₁ -O ₄ -H ₅ -N ₉		-9.8	-120.2	-123.4			
φ H ₅ -O ₄ -H ₇ -O ₈			0.0	-0.4			
φ O ₄ -H ₇ -N ₉ -O ₈			1.6	0.4			
φ C ₁ -O ₄ -H ₅ -O ₈					-23.6	-158.2	-71.2
φ O ₄ -H ₅ -O ₈ -N ₉					-6.7	8.0	-18.6
φ C ₁ -O ₄ -H ₁₀ -N ₉						90.5	

Table S3. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}) and intensities (I , km mol^{-1}) for **HA** and **HA-d**.

NH ₂ OH			ND ₂ OD			NHDOD			ND ₂ OH		
HA			HA-d₁			HA-d₂			HA-d₃		
ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I
3872	3675	54	2821	2716	29	3565	3384	4	3872	3675	54
3609	3422	7	2661	2558	4	2821	2716	29	2661	2558	4
3519	3350	1	2542	2455	0	2600	2504	2	2542	2455	0
1683	1617	18	1219	1184	9	1516	1465	13	1402	1386	43
1416	1361	28	1076	1043	4	1216	1168	32	1217	1182	12
1337	1294	0	987	962	0	1055	1025	6	989	964	0
1163	1124	128	943	912	48	947	917	54	969	936	49
930	894	11	842	819	43	898	868	30	858	836	31
434	407	179	316	301	95	330	314	105	401	378	149

Table S4. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}), intensities (I , km mol^{-1}) and potential energy distribution (PED) for **HK** and **HK-d**.

HK			
ν	ν_{anh}	I	PED ^{a,b}
3850	3656	71	νOH (99)
3248	3115	18	νCH (99)
2174	2123	379	$\nu_{as}\text{OCC}$ (99)
1429	1393	12	δCH (48) + $\nu_s\text{OCC}$ (27) + $\nu\text{C-O}$ (16) + δOH (48)
1285	1242	40	δOH (73) + τCH (27)
1175	1151	71	$\nu\text{C-O}$ (33) + δOH (20) + δCH (19) + $\nu_s\text{OCC}$ (27)
1027	992	22	$\nu\text{C-O}$ (46) + $\nu_s\text{OCC}$ (26) + δOCC (23)
682	671	5	δOCC (73) + $\nu\text{C-O}$ (10)
575	580	38	γCH (44) + γOCC (31) + γOH (24)
488	450	44	γOCC (51) + γCH (48)
299	326	115	γOH (74) + γOCC (10) + γCH (10)
226	163	1	δOCC (90?)
HK-d (OD)			
3248	3114	18	νCH (99)
2804	2701	39	νOD (100)
2174	2128	379	$\nu_{as}\text{OCC}$ (99)
1413	1381	30	δCH (56) + $\nu_s\text{OCC}$ (27) + $\nu\text{C-O}$ (16)
1193	1172	25	δCH (37) + $\nu\text{C-O}$ (33) + $\nu_s\text{OCC}$ (29)
1026	988	27	$\nu\text{C-O}$ (47) + δOCC (23) + $\nu_s\text{OCC}$ (25)
955	936	37	δOD (92)
679	666	4	δOCC (74) + $\nu\text{C-O}$ (10)
563	577	28	γCH (45) + γOCC (36) + γOD (16)
485	445	44	γOCC (51) + γCH (48)
246	327	47	δOCC (64) + γOD (31)
205	102	20	γOD (43) + δOCC (42) + γOCC (7)

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching; δ , bending; γ , rocking; τ , torsion; s, symmetric; as, asymmetric.

^b Potential energy distribution (PED) values greater than 10 % are given.

Table S5. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}) and intensities (I , km mol^{-1}) for **HK-NA** complexes (**I_{HKH}**-**VI_{HKH}**).

I_{HKH}			II_{HKH}			III_{HKH}			IV_{HKH}			V_{HKH}			VI_{HKH}		
ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I
3732	3533	365	3763	3581	231	3776	3591	188	3863	3667	70	3863	3668	66	3862	3668	69
3601	3412	15	3606	3418	15	3607	3419	15	3673	3488	548	3678	3502	589	3659	3486	560
3517	3351	48	3522	3359	82	3521	3350	16	3594	3416	25	3597	3468	14	3599	3433	10
3487	3260	697	3500	3259	647	3478	3239	723	3496	3328	14	3503	3301	4	3506	3330	0
3217	3082	22	3237	3101	28	3240	3104	26	3226	3093	19	3240	3105	24	3238	3102	20
2161	2114	431	2169	2122	416	2165	2118	375	2163	2115	391	2169	2123	405	2163	2116	360
1678	1620	21	1679	1617	22	1678	1615	21	1685	1621	4	1691	1628	16	1688	1623	15
1508	1450	4	1506	1444	39	1505	1436	30	1464	1416	6	1465	1410	17	1463	1417	1
1468	1407	29	1465	1407	9	1467	1400	25	1402	1349	34	1405	1362	38	1402	1350	48
1382	1353	47	1373	1317	126	1372	1326	113	1361	1319	22	1372	1315	31	1355	1313	1
1325	1287	0	1322	1284	3	1323	1284	2	1350	1291	32	1347	1283	100	1346	1290	47
1192	1159	128	1189	1164	42	1189	1165	52	1182	1167	144	1189	1178	24	1183	1161	56
1178	1154	27	1184	1150	156	1183	1149	133	1178	1126	43	1182	1127	209	1174	1125	142
1029	996	17	1030	1026	26	1030	1033	24	1031	993	16	1031	1027	25	1031	989	18
947	907	9	946	903	12	947	904	11	925	887	13	922	882	12	926	888	9
832	752	119	830	720	189	842	759	134	713	623	102	688	680	17	749	616	119
688	672	11	685	673	3	683	672	4	686	677	6	669	590	93	685	678	5
584	568	64	549	555	61	558	551	72	559	548	69	536	543	50	556	540	83
513	515	32	533	445	78	509	433	69	487	477	15	492	467	29	481	469	23
482	412	42	481	459	30	481	467	27	449	401	149	456	376	141	457	408	129
271	255	3	319	287	1	314	280	1	235	223	6	246	228	11	240	226	11
233	219	7	251	231	9	256	238	21	199	189	5	224	205	9	217	200	2
217	208	7	227	207	21	224	211	3	180	167	1	175	79	2	151	0	7
188	167	0	122	101	4	141	118	2	132	84	8	123	169	2	97	154	7
137	119	1	112	104	7	93	76	9	106	89	1	89	35	10	83	95	3
53	72	2	36	32	0	45	44	5	44	41	1	37	31	0	27	34	3
39	16	9	21	10	1	24	17	0	38	31	2	11	11	1	23	24	0

Table S6. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}) and intensities (I , km mol^{-1}) for deuterated hydroxylamine -hydroxyketene complexes ($\text{I}_{\text{HKH-d}}\text{-VI}_{\text{HKH-d}}$).

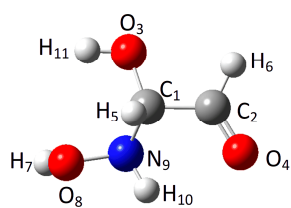
ND ₂ OD H(OH)CCO			NHDOD H(OD)CCO			NDHOD H(OD)CCO			ND ₂ OH H(OD)CCO			ND ₂ OD H(OH)CCO			NHDOD H(OD)CCO			NDHOD H(OD)CCO			ND ₂ OH H(OD)CCO		
$\text{I}_{\text{HKH-d1}}$			$\text{I}_{\text{HKH-d2a}}$			$\text{I}_{\text{HKH-d2b}}$			$\text{I}_{\text{HKH-d3}}$			$\text{II}_{\text{HKH-d1}}$			$\text{II}_{\text{HKH-d2a}}$			$\text{II}_{\text{HKH-d2b}}$			$\text{II}_{\text{HKH-d3}}$		
ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I
3491	3272	821	3558	3375	9	3560	3377	9	3731	3533	305	3506	3273	809	3562	3379	10	3566	3383	9	3761	3580	167
3217	3082	23	3217	3082	17	3217	3082	17	3217	3082	16	3237	3101	27	3237	3101	20	3237	3101	20	3237	3100	20
2719	2614	138	2720	2615	184	2720	2615	184	2655	2551	8	2740	2644	71	2742	2646	119	2742	2645	119	2660	2556	8
2655	2551	8	2597	2498	4	2595	2500	5	2549	2472	261	2660	2556	8	2602	2503	5	2599	2499	4	2559	2417	335
2539	2451	2	2544	2432	382	2544	2431	381	2536	2410	148	2543	2454	2	2554	2437	379	2554	2438	381	2540	2474	75
2160	2113	434	2160	2114	441	2160	2115	441	2160	2116	438	2169	2122	418	2168	2122	429	2168	2122	428	2168	2122	427
1495	1434	16	1508	1462	13	1508	1463	13	1473	1417	36	1474	1436	12	1508	1465	15	1510	1464	15	1485	1437	67
1382	1337	41	1402	1373	26	1402	1373	25	1402	1374	25	1376	1315	115	1417	1387	39	1417	1385	39	1416	1386	44
1215	1183	9	1227	1188	26	1228	1188	27	1214	1182	9	1216	1183	11	1222	1182	25	1227	1186	27	1215	1183	13
1179	1160	49	1192	1170	23	1192	1170	23	1192	1170	21	1190	1166	62	1194	1174	26	1194	1174	29	1194	1174	27
1111	1078	4	1084	1048	16	1080	1044	10	1073	1028	49	1121	1080	12	1098	1064	23	1086	1051	22	1052	1035	115
1029	1002	19	1073	1029	45	1073	1030	51	1027	1010	11	1030	986	21	1046	991	109	1048	1039	107	1022	1002	2
978	954	1	1027	992	11	1027	992	11	980	957	0	977	954	1	1022	976	2	1022	1003	2	979	960	4
960	932	32	962	941	34	964	944	34	974	945	35	964	935	35	965	942	46	968	945	48	977	943	39
874	851	46	923	886	27	924	886	25	888	857	36	866	841	79	917	881	36	917	881	26	878	848	40
814	740	89	685	675	10	685	675	10	686	674	13	822	729	172	683	671	3	683	670	3	683	673	3
687	674	11	632	600	70	632	599	76	645	614	92	685	672	4	621	577	91	619	580	98	627	578	108
575	567	65	552	533	61	553	533	55	550	517	56	547	545	28	535	510	27	535	509	28	535	517	23
495	475	35	493	477	35	493	476	37	506	537	26	487	463	34	486	469	37	486	469	38	517	391	87
372	345	25	372	347	21	372	347	20	471	380	30	388	341	56	392	357	59	396	367	54	475	507	32
229	223	7	234	217	2	235	234	5	228	223	7	268	257	2	271	249	0	284	262	4	267	252	1
214	202	6	227	226	6	221	215	8	210	202	2	233	219	5	241	227	6	237	230	5	236	224	7
206	189	2	207	197	6	206	186	2	206	194	5	209	187	18	220	202	22	207	185	19	208	188	20
176	160	1	175	152	1	180	158	0	176	153	0	119	100	4	119	100	4	119	102	4	122	99	4
132	118	1	132	118	1	132	117	1	136	118	1	105	95	6	105	96	6	107	97	7	104	96	6
52	71	1	52	74	1	53	69	2	52	67	1	35	38	0	36	39	0	35	32	0	35	40	0
36	13	8	37	12	8	37	18	8	36	19	8	20	10	1	20	9	1	20	16	1	20	6	1

Table S6. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}) and intensities (I , km mol^{-1}) for deuterated hydroxylamine -hydroxyketene complexes (**I**_{NKH-d}-**VI**_{NKH-d})- continuation.

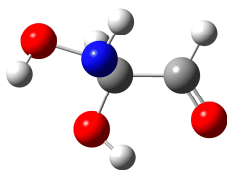
ND ₂ OD H(OH)CCO			NHDOD H(OD)CCO			NDHOD H(OD)CCO			ND ₂ OH H(OD)CCO			ND ₂ OD H(OH)CCO			NHDOD H(OD)CCO			NDHOD H(OD)CCO			ND ₂ OH H(OD)CCO		
III _{NKH-d1}			III _{NKH-d2a}			III _{NKH-d2b}			III _{NKH-d3}			IV _{NKH-d1}			IV _{NKH-d2a}			IV _{NKH-d2b}			IV _{NKH-d3}		
ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I
3481	3247	802	3565	3382	10	3565	3383	9	3774	3592	140	3673	3486	533	3529	3356	43	3564	3383	8	3863	3667	77
3240	3104	26	3241	3104	19	3241	3104	19	3241	3103	19	3226	3093	19	3226	3093	16	3226	3093	17	3226	3093	17
2749	2652	58	2751	2654	98	2751	2654	98	2660	2556	8	2815	2710	43	2815	2710	38	2815	2710	38	2675	2579	282
2660	2556	8	2601	2502	5	2600	2500	3	2548	2477	114	2650	2549	17	2675	2579	278	2675	2579	282	2650	2549	12
2543	2455	2	2537	2420	386	2537	2420	390	2534	2396	296	2527	2446	8	2600	2505	2	2574	2479	16	2527	2445	7
2164	2118	374	2164	2118	380	2164	2118	380	2164	2118	381	2163	2118	391	2163	2118	394	2162	2118	395	2162	2118	394
1480	1426	24	1508	1463	16	1509	1464	16	1479	1431	52	1463	1418	8	1529	1477	5	1514	1467	7	1412	1381	27
1379	1328	104	1412	1381	38	1412	1381	38	1410	1380	41	1354	1300	56	1412	1381	30	1412	1381	30	1385	1312	49
1216	1182	11	1223	1184	27	1226	1186	29	1215	1181	13	1220	1187	2	1234	1179	32	1223	1177	31	1217	1183	5
1189	1165	57	1195	1172	28	1194	1171	31	1195	1172	28	1181	1156	55	1191	1169	25	1191	1170	25	1191	1169	26
1117	1080	11	1094	1056	22	1087	1050	16	1057	1030	109	1066	1035	7	1053	1021	7	1054	1025	11	1045	1012	55
1030	989	22	1049	1010	99	1053	1012	99	1025	1007	3	1031	991	18	1045	1009	53	1045	1009	53	1013	985	2
977	954	0	1024	1028	2	1024	1029	3	980	957	0	1001	975	1	1013	976	3	1012	976	2	1003	972	1
964	933	33	966	944	43	966	944	43	977	949	40	941	917	56	944	929	62	948	931	65	968	938	54
866	848	76	918	882	32	917	880	27	879	847	38	850	818	38	900	857	20	901	858	21	866	842	24
834	747	112	682	671	3	682	673	3	682	670	3	706	614	85	684	673	5	684	673	5	684	675	5
683	670	3	634	599	51	632	587	55	636	591	61	686	682	7	584	565	40	585	566	41	587	564	39
551	543	48	537	518	63	536	515	68	544	526	86	558	543	63	504	484	78	503	485	77	513	479	127
485	470	22	483	472	19	483	472	19	488	501	34	484	467	23	472	428	27	472	428	27	481	450	21
376	333	50	380	339	52	386	353	46	476	376	41	334	314	85	344	324	85	345	325	88	401	369	82
261	244	4	263	237	2	279	256	4	265	250	2	234	225	5	232	224	5	232	224	5	232	224	6
240	223	15	248	232	21	241	224	17	240	227	16	193	180	4	191	177	4	190	177	4	194	184	5
205	189	3	216	207	2	204	192	3	205	188	4	151	137	2	157	144	2	154	123	1	151	136	1
137	117	2	137	115	2	137	117	2	139	110	2	113	98	4	118	102	5	120	138	6	119	114	6
87	71	8	87	75	8	88	73	8	87	75	8	101	89	1	105	88	1	102	78	1	101	84	1
42	50	4	43	50	4	44	50	4	43	50	4	43	34	1	43	23	1	43	23	1	43	22	1
24	9	0	24	10	0	24	11	0	24	8	0	36	29	1	36	33	1	37	28	1	37	33	2

Table S6. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}) and intensities (I , km mol^{-1}) for deuterated hydroxylamine -hydroxyketene complexes ($\text{I}_{\text{HKH-d}}$ - $\text{VI}_{\text{HKH-d}}$)- continuation.

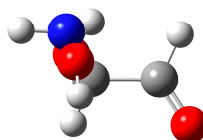
ND ₂ OD H(OH)CCO			NHDOD H(OD)CCO			NDHOD H(OD)CCO			ND ₂ OH H(OD)CCO			ND ₂ OD H(OH)CCO			NHDOD H(OD)CCO			NDHOD H(OD)CCO			ND ₂ OH H(OD)CCO		
$\text{V}_{\text{HKH-d1}}$			$\text{V}_{\text{HKH-d2a}}$			$\text{V}_{\text{HKH-d2b}}$			$\text{V}_{\text{HKH-d3}}$			$\text{VI}_{\text{HKH-d1}}$			$\text{VI}_{\text{HKH-d2a}}$			$\text{VI}_{\text{HKH-d2b}}$			$\text{VI}_{\text{HKH-d3}}$		
ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I
3678	3499	570	3567	3385	7	3537	3367	26	3863	3667	72	3659	3478	545	3566	3385	7	3543	3371	8	3862	3667	77
3240	3105	24	3240	3104	20	3240	3104	20	3240	3104	20	3238	3103	20	3238	3103	17	3238	3103	17	3238	3103	17
2814	2710	41	2814	2710	36	2814	2710	36	2680	2588	310	2814	2710	45	2814	2710	38	2814	2710	38	2665	2574	288
2652	2551	12	2680	2588	308	2680	2588	303	2652	2551	5	2654	2553	7	2665	2574	292	2665	2574	290	2654	2553	5
2532	2453	4	2579	2487	7	2602	2508	2	2532	2452	3	2534	2452	1	2584	2495	2	2601	2506	3	2534	2452	0
2169	2123	406	2168	2123	410	2168	2123	409	2168	2123	410	2163	2116	360	2163	2117	363	2163	2117	363	2163	2117	362
1460	1415	14	1516	1469	14	1539	1486	16	1415	1383	37	1461	1413	4	1520	1471	12	1529	1475	8	1415	1381	31
1364	1302	150	1415	1386	36	1415	1385	36	1383	1345	39	1350	1304	61	1414	1382	33	1414	1381	32	1385	1313	49
1225	1192	9	1227	1182	34	1241	1196	40	1221	1187	12	1222	1188	8	1225	1176	43	1223	1172	47	1219	1184	12
1189	1166	70	1195	1175	23	1195	1174	23	1195	1174	26	1183	1156	55	1191	1168	29	1191	1168	31	1191	1168	30
1065	1034	8	1066	1034	26	1054	1023	11	1040	999	101	1066	1035	6	1048	1018	12	1059	1031	10	1043	1006	52
1031	1028	22	1033	997	64	1036	1001	101	1021	984	9	1031	990	17	1043	1004	47	1042	1004	47	1010	983	4
1005	975	2	1015	973	46	1018	976	37	1004	971	22	1000	971	2	1010	983	4	1010	982	4	1001	975	2
934	921	57	944	941	83	939	943	65	965	956	72	939	918	56	946	939	69	941	935	61	966	937	59
855	814	46	905	843	20	901	837	21	870	824	28	848	814	39	903	849	22	898	846	27	864	835	27
687	684	12	682	672	2	682	671	2	682	669	1	746	625	115	684	674	4	684	676	4	684	674	4
664	575	93	571	559	31	571	559	31	573	554	32	685	683	5	588	567	26	588	566	26	589	561	23
535	516	44	490	473	40	490	473	39	490	472	36	554	539	65	511	482	100	512	483	102	520	473	135
485	469	22	453	393	53	453	392	52	476	455	99	480	470	19	475	437	12	475	439	12	475	460	8
342	309	91	348	311	91	349	312	90	411	306	78	340	312	78	352	327	86	352	323	84	423	374	96
243	226	8	239	227	8	239	226	9	240	228	10	237	224	10	235	225	10	235	225	10	237	224	10
220	200	9	219	199	10	221	203	10	220	203	10	211	195	1	208	199	2	209	196	2	211	193	2
135	84	1	150	95	1	145	93	1	136	85	1	123	73	8	132	140	7	127	130	6	126	94	8
114	174	1	115	167	1	118	170	1	119	177	2	83	156	3	86	79	3	88	42	6	87	-8	4
83	33	10	84	47	9	85	40	10	84	21	9	79	1	5	78	31	5	82	87	3	79	147	4
36	23	0	36	12	0	36	15	0	37	40	0	26	56	2	27	21	2	27	17	2	27	46	2
10	9	1	10	12	1	10	11	1	10	7	1	22	16	0	23	39	0	22	29	0	22	37	0



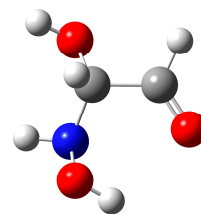
$I_{\text{HHA}}(0.00)$



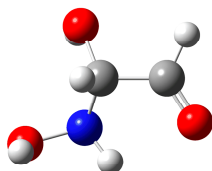
$II_{\text{HHA}}(3.82)$



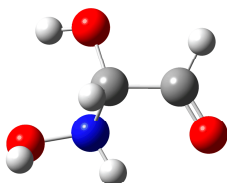
$III_{\text{HHA}}(13.80)$



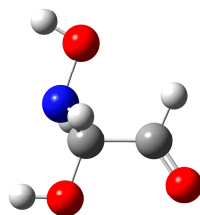
$IV_{\text{HHA}}(16.14)$



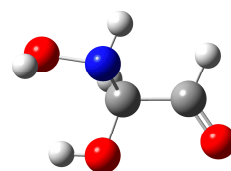
$V_{\text{HHA}}(17.17)$



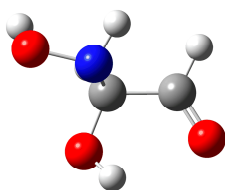
$VI_{\text{HHA}}(17.46)$



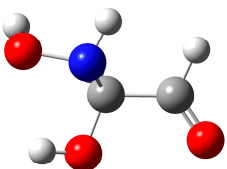
$VII_{\text{HHA}}(17.93)$



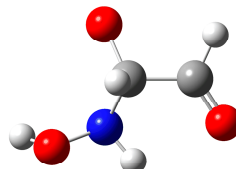
$VIII_{\text{HHA}}(18.65)$



$IX_{\text{HHA}}(28.52)$



$X_{\text{HHA}}(38.55)$



$XI_{\text{HHA}}(49.89)$

Figure S3. The optimized structures of the hydroxy(hydroxyamino)acetaldehyde, **HHA**. The computed $\Delta E(\text{ZPE})$ energies of **HHA** conformers in respect to the energy of the most stable conformer, I_{HHA} , in kJ mol^{-1} are given in parentheses.

Table S7. Selected geometrical parameters of the conformers of (hydroxy(hydroxyamino)acetaldehyde (**I_{HNA}**- **XI_{HNA}**). The atoms are numbered in the same way as presented in Fig. S3. Bond distances are given in Å, angles in °.

<i>Parameter</i>	I_{HNA}	II_{HNA}	III_{HNA}	IV_{HNA}	V_{HNA}	VI_{HNA}	VII_{HNA}	VIII_{HNA}	IX_{HNA}	X_{HNA}	XI_{HNA}
r C ₁ -C ₂	1.519	1.522	1.520	1.523	1.530	1.521	1.522	1.520	1.526	1.522	1.526
r C ₁ -O ₃	1.405	1.393	1.419	1.411	1.408	1.405	1.396	1.392	1.388	1.392	1.412
r C ₂ -O ₄	1.214	1.214	1.214	1.212	1.214	1.214	1.212	1.208	1.212	1.207	1.213
r C ₁ -H ₅	1.097	1.093	1.093	1.097	1.098	1.102	1.093	1.099	1.098	1.106	1.092
r C ₂ -H ₆	1.099	1.101	1.102	1.101	1.100	1.099	1.101	1.106	1.102	1.106	1.102
r O ₈ -H ₇	0.961	0.961	0.961	0.963	0.967	0.968	0.961	0.961	0.967	0.968	0.959
r O ₈ -N ₉	1.449	1.442	1.446	1.445	1.426	1.434	1.446	1.449	1.427	1.435	1.439
r N ₉ -H ₁₀	1.016	1.015	1.014	1.013	1.014	1.015	1.016	1.016	1.016	1.015	1.013
r O ₃ -H ₁₁	0.961	0.966	0.961	0.959	0.963	0.962	0.962	0.961	0.965	0.963	0.962
θ C ₂ -C ₁ -O ₃	107.1	111.4	108.9	106.7	110.9	107.5	108.9	109.7	111.9	110.2	110.6
θ C ₁ -C ₂ -O ₄	122.1	121.6	122.9	123.7	122.8	121.8	124.3	124.3	121.6	124.3	123.3
θ C ₂ -C ₁ -H ₅	108.7	110.1	109.4	107.5	107.5	108.2	108.6	107.9	109.2	106.7	108.7
θ O ₃ -C ₁ -H ₅	110.4	107.6	112.1	111.8	106.0	110.1	84.7	110.8	116.9	110.5	105.6
θ N ₉ -C ₁ -H ₅	110.6	110.7	112.9	111.1	113.1	111.4	106.0	110.1	111.8	110.7	111.9
θ C ₁ -C ₂ -H ₆	115.3	117.0	114.5	114.3	114.7	115.4	113.9	114.3	106.3	114.2	114.3
θ O ₄ -C ₂ -H ₆	122.6	121.4	122.4	122.0	122.5	122.8	121.8	121.3	121.4	121.5	122.4
θ H ₇ -O ₈ -N ₉	101.9	101.9	102.3	101.1	106.7	106.7	102.1	101.9	106.9	106.8	102.1
θ O ₈ -N ₉ -H ₁₀	104.7	102.5	104.7	103.1	108.5	108.1	104.1	103.2	106.4	106.7	104.6
θ C ₁ -N ₉ -H ₁₀	106.8	109.2	107.2	108.0	109.3	108.9	107.7	108.0	109.8	110.2	107.7
θ C ₁ -O ₃ -H ₁₁	107.4	106.6	107.8	109.1	106.0	107.0	107.0	106.7	107.1	106.5	105.6
φ O ₃ -C ₁ -C ₂ -O ₄	-164.9	-7.6	102.2	-138.1	-159.4	-167.9	2.3	-168.8	-12.6	9.3	-151.5
φ O ₄ -C ₂ -C ₁ -H ₅	75.8	-126.9	-20.6	101.7	85.1	73.2	-121.8	-108.2	-130.0	-110.8	93.1
φ H ₅ -C ₁ -C ₂ -H ₆	-103.5	54.3	163.1	-77.7	-94.1	-106.6	59.7	70.5	51.5	67.6	-86.6
φ N ₉ -C ₁ -C ₂ -H ₆	136.7	-65.5	39.2	161.5	143.7	132.9	-56.8	-48.0	-68.7	-51.2	151.6
φ O ₃ -C ₁ -C ₂ -H ₆	15.8	173.6	-74.1	42.4	21.2	12.3	-176.2	-168.8	168.9	-172.4	28.8
φ N ₉ -C ₁ -O ₃ -H ₁₁	66.6	-95.5	163.2	93.7	-25.8	43.0	56.0	67.9	-81.8	41.2	-42.7
φ O ₈ -N ₉ -C ₁ -H ₅	44.9	43.2	-47.6	-39.9	40.7	47.9	-56.0	50.9	48.6	53.1	30.3
φ O ₈ -N ₉ -C ₁ -O ₃	-78.9	-76.3	-169.5	-164.3	-78.8	-75.7	-178.2	-72.5	-70.7	-70.1	-87.9
φ H ₅ -C ₁ -N ₉ -H ₁₀	-66.2	-67.1	63.3	70.0	-79.5	-69.8	-167.7	-59.0	-68.7	-63.5	-82.5
φ O ₃ -C ₁ -N ₉ -H ₁₀	170.0	173.4	-58.7	-54.3	161.0	-75.6	70.2	177.7	171.7	173.3	159.3
φ C ₁ -N ₉ -O ₈ -H ₇	130.8	104.8	-128.9	-99.2	-58.5	-62.2	124.1	127.5	-51.1	-59.8	112.1
φ H ₇ -O ₈ -N ₉ -H ₁₀	-116.6	-140.2	118.4	147.5	62.2	56.0	-121.9	-119.2	68.3	59.0	-133.1

Table S8. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}), intensities (I , km mol^{-1}) and PED for **I_{HHA}** and **I_{HHA-d}**.

I_{HHA}			
ν	ν_{anh}	I	PED ^{a,b}
3865	3676	63	$\nu(\text{C})\text{OH}$ (100)
3854	3656	71	$\nu(\text{N})\text{OH}$ (100)
3519	3339	16	νNH (100)
3021	2852	52	$\nu\text{CH}_{\text{ald}}$ (97)
3017	2911	36	νCH (92)
1751	1718	85	$\nu\text{C}=\text{O}$ (85)
1496	1438	5	δNH (55) + δCH (10)
1426	1393	7	δNH (25) + $\delta\text{CH}_{\text{ald}}$ (23) + δCH (23)
1400	1358	32	δNOH (30) + δCH (29) + δNH (11)
1397	1364	24	$\delta\text{CH}_{\text{ald}}$ (59) + δCOH (11) + δCH (11)
1347	1293	29	δCH (38) + δNOH (37)
1232	1208	50	δCH (47) + δCOH (44)
1208	1169	55	$\nu\text{C}-\text{O}$ (35) + γNH (20) + δCCN (16) + $\nu\text{C}-\text{N}$ (14)
1093	1060	72	$\nu\text{C}-\text{N}$ (34) + γNH (16)
1053	1036	10	$\gamma\text{CH}_{\text{ald}}$ (31) + $\nu\text{C}-\text{C}$ (11) + δCNO (10)
1025	984	94	$\nu\text{C}-\text{O}$ (24) + γNH (18) + $\nu\text{C}-\text{C}$ (16) + $\nu\text{N}-\text{O}$ (16)
953	916	34	$\nu\text{N}-\text{O}$ (38) + γNH (23)
826	806	36	$\nu\text{C}-\text{N}$ (19) + $\nu\text{N}-\text{O}$ (19) + $\gamma\text{CH}_{\text{ald}}$ (19) + γNH (14)
639	637	25	δCCO (37) + δCCN (16)
556	543	8	τNCO (45) + δCCN (15)
475	470	14	δCCO (33) + δCNO (21) + $\nu\text{C}-\text{C}$ (20)
403	381	48	δNOH (68) + δCOH (11)
294	389	50	δCCO (38) + γOH (24)
268	152	116	$\gamma(\text{C})\text{OH}$ (43) + $\gamma(\text{N})\text{OH}$ (24) + δCNO (11)
234	232	9	δCCN (61) + δCCO (14)
127	140	5	$\tau\text{C}-\text{C}$ (49) + $\tau\text{N}-\text{O}$ (18) + δCNO (11)
87	66	8	$\tau\text{N}-\text{O}$ (48) + $\tau\text{C}-\text{C}$ (33)

I_{HHA-d}			
ν	ν_{anh}	I	PED ^{a,b}
3021	2857	52	$\nu\text{CH}_{\text{ald}}$ (97)
3017	2902	35	νCH (97)
2813	2713	39	$\nu(\text{C})\text{OD}$ (100)
2808	2702	39	$\nu(\text{N})\text{OD}$ (100)
2573	2478	10	νND (98)
1751	1719	84	$\nu\text{C}=\text{O}$ (85)
1427	1397	22	$\delta\text{CH}_{\text{ald}}$ (42) + δCH (41)
1382	1347	3	$\delta\text{CH}_{\text{ald}}$ (45) + δCH (45)
1367	1325	5	δCH (59) + $\nu\text{C}-\text{C}$ (12)
1185	1143	67	$\nu\text{C}-\text{N}$ (47) + $\nu\text{C}-\text{O}$ (24)
1167	1136	29	$\nu\text{C}-\text{O}$ (37) + δND (28)
1120	1094	19	$\gamma\text{CH}_{\text{ald}}$ (28) + $\gamma\text{C}-\text{C}$ (15) + δCOD (12) + δCCO (11) + δCH (10)
1042	1015	3	δND (44) + δNOD (25)
1014	990	8	νNO (29) + $\gamma\text{CH}_{\text{ald}}$ (21) + δNOD (12)
943	913	56	νNO (45) + δNOD (43)
897	884	56	δCOD (59) + $\gamma\text{CH}_{\text{ald}}$ (12)
830	816	5	δCNO (22) + $\nu\text{C}-\text{N}$ (16) + $\nu\text{C}-\text{C}$ (11) + $\gamma\text{CH}_{\text{ald}}$ (11)
776	750	58	γND (49) + δCNO (10) + νNO (10)
618	616	23	γCCO (42) + γCCN (11)
532	515	5	δNCO (45) + δCCN (12) + γND (10)
466	458	10	δCCO (29) + δCNO (23) + $\nu\text{C}-\text{C}$ (19)
296	302	34	$\gamma\text{OD}_{11}(66)$ + $\gamma\text{OD}_7(10)$
278	262	5	δCCO (43) + δCNO (20) + $\delta\text{CC}=\text{O}$ (13)
224	218	6	δCCN (62) + $\delta\text{CC}=\text{O}$ (13) + δCNO (10)
202	192	89	$\gamma\text{OD}_7(63)$ + $\gamma\text{OD}_{11}(27)$
121	134	4	$\tau\text{C}-\text{C}$ (46) + $\tau\text{N}-\text{O}$ (23)
85	60	7	$\tau\text{N}-\text{O}$ (46) + $\tau\text{C}-\text{C}$ (35)

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching;

δ , bending; γ , rocking; τ , torsion; s, symmetric; as, asymmetric.

^b Potential energy distribution (PED) values greater than 10 % are given.

Table S9. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}), intensities (I , km mol^{-1}) and PED for Π_{HHA} and $\Pi_{\text{HHA-d}}$.

Π_{HHA}			
ν	ν_{anh}	I	PED ^{a,b}
3855	3655	73	$\nu(\text{N})\text{OH}$ (100)
3773	3578	71	$\nu(\text{C})\text{OH}$ (100)
3522	3344	5	νNH (100)
3065	2927	27	νCH (99)
2993	2838	61	$\nu\text{CH}_{\text{ald}}$ (99)
1747	1720	87	$\nu\text{C}=\text{O}$ (85)
1516	1469	2	δNH (73) + δNOH (34)
1457	1416	46	δCOH (73) + δCH (34)
1420	1394	12	$\delta\text{CH}_{\text{ald}}$ (57) + δCH (19) + δNOH (11)
1376	1330	25	δNOH (33) + $\delta\text{CH}_{\text{ald}}$ (18) + δNH (17) + δCOH (13)
1337	1299	37	δCH (50) + δNOH (21)
1297	1249	29	δCH (35) + δCOH (16) + $\nu\text{C-O}$ (16)
1193	1162	85	$\nu\text{C-O}$ (31) + δCH (13) + δCOH (13) + $\nu\text{C-N}$ (11)
1071	1036	29	$\nu\text{C-N}$ (37) + $\gamma\text{CH}_{\text{ald}}$ (17) + δCCN (11)
1032	998	59	$\nu\text{N-O}$ (31) + $\gamma\text{CH}_{\text{ald}}$ (12) + δCNO (11)
977	953	14	γNH (30) + $\nu\text{C-C}$ (18) + $\gamma\text{CH}_{\text{ald}}$ (14) + $\nu\text{C-N}$ (11) + δCCO (11)
905	871	68	γNH (26) + $\nu\text{N-O}$ (25) + $\nu\text{C-O}$ (14) + $\nu\text{C-C}$ (13) + δCNO (11)
831	806	31	γNH (22) + $\nu\text{N-O}$ (17) + $\nu\text{C-C}$ (13) + $\gamma\text{CH}_{\text{ald}}$ (10) + $\nu\text{C-N}$ (10)
764	742	20	$\delta\text{CC}=\text{O}$ (28) + $\delta\text{CC-O}$ (28)
559	546	16	δNCO (62) + γNH (14)
425	433	37	$\gamma(\text{C})\text{OH}$ (19) + δCNO (18) + δCCN (17) + $\delta\text{CC}=\text{O}$ (12)
367	329	50	$\gamma(\text{C})\text{OH}$ (58) + δCNO (14)
314	455	85	$\gamma(\text{N})\text{OH}$ (50) + δCNO (18) + δCCN (17)
287	251	42	$\delta\text{CC-O}$ (36) + $\delta\text{CC}=\text{O}$ (27)
250	100	21	δNCO (24) + $\gamma(\text{N})\text{OH}$ (22) + $\gamma(\text{C})\text{OH}$ (14) + $\delta\text{CC-O}$ (11)
112	115	11	τCN (61) + γNCO (24)
102	94	2	$\tau\text{C-C}$ (50) + $\gamma(\text{C})\text{OH}$ (35)

$\Pi_{\text{HHA-d}}$			
ν	ν_{anh}	I	PED ^{a,b}
3066	2925	26	νCH (99)
2993	2860	63	$\nu\text{CH}_{\text{ald}}$ (98)
2808	2702	40	$\nu(\text{C})\text{OD}$ (100)
2745	2642	41	$\nu(\text{N})\text{OD}$ (100)
2576	2484	4	νND (99)
1747	1711	88	$\nu\text{C}=\text{O}$ (85)
1417	1388	9	$\delta\text{CH}_{\text{ald}}$ (82)
1406	1367	12	δCH (72)
1332	1302	2	δCH (75)
1208	1176	40	$\nu\text{C-O}$ (55)
1143	1101	29	$\nu\text{C-N}$ (40) + δND (38)
1098	1070	7	$\delta\text{CH}_{\text{ald}}$ (20) + δNOD (19) + δND (16) + δCOD (16)
1076	1048	12	δNOD (29) + δCOD (14) + $\nu\text{N-O}$ (12) + $\gamma\text{CH}_{\text{ald}}$ (10)
997	974	41	δCOD (32) + $\gamma\text{CH}_{\text{ald}}$ (15) + $\nu\text{N-O}$ (12)
944	919	62	δNOD (44) + $\nu\text{N-O}$ (39)
917	892	44	$\nu\text{C-C}$ (29) + $\nu\text{N-O}$ (17) + δCOD (14) + $\nu\text{C-N}$ (12)
846	834	16	$\gamma\text{CH}_{\text{ald}}$ (19) + $\nu\text{C-N}$ (14) + $\nu\text{C-C}$ (14) + $\nu\text{C-O}$ (13) + $\delta\text{CC}=\text{O}$ (12)
739	729	35	γND (47) + δCNO (24) + $\delta\text{CC}=\text{O}$ (12)
731	703	21	γND (24) + $\delta\text{CC-O}$ (25) + $\delta\text{CC}=\text{O}$ (15)
524	517	14	δNCO (49) + γND (30)
411	403	12	δCNO (27) + δCCN (22) + $\nu\text{C-C}$ (13)
318	328	12	$\delta\text{CC-O}$ (31) + $\gamma(\text{C})\text{OD}$ (25) + δCNO (17) + $\delta\text{CC}=\text{O}$ (11)
286	291	19	δCCN (33) + δCNO (22) + $\tau\text{C-C}$ (13) + $\gamma(\text{N})\text{OD}$ (11)
242	227	75	$\gamma(\text{C})\text{OD}$ (39) + $\delta\text{CC-O}$ (20) + $\gamma(\text{N})\text{OD}$ (13)
195	158	21	$\gamma(\text{N})\text{OD}$ (49) + $\gamma(\text{C})\text{OD}$ (16) + δCCN (12)
105	102	9	$\tau\text{C-N}$ (60) + δNCO (12) + $\tau(\text{N})\text{OD}$ (11)
99	92	3	$\tau\text{C-C}$ (46) + $\gamma(\text{C})\text{OD}$ (38)

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching;

δ , bending; γ , rocking; τ , torsion; s, symmetric; as, asymmetric.

^b Potential energy distribution (PED) values greater than 10 % are given.

Table S10. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}) and intensities (I , km mol^{-1}) for conformers of **HHA** (**I_{HHA}**-**VI_{HHA}**).

I_{HHA}			II_{HHA}			III_{HHA}			IV_{HHA}			V_{HHA}			VI_{HHA}		
ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I
3865	3676	63	3855	3655	73	3865	3677	73	3885	3695	66	3828	3638	64	3843	3656	74
3854	3656	71	3773	3578	71	3854	3656	66	3828	3628	71	3746	3545	10	3730	3531	9
3519	3339	16	3522	3344	5	3531	3350	9	3546	3364	5	3535	3357	20	3528	3351	14
3021	2852	52	3065	2927	27	3069	2936	29	3022	2896	40	3014	2921	49	3027	2872	49
3017	2911	36	2993	2838	61	2989	2834	58	2996	2837	64	3010	2804	46	2959	2847	61
1751	1718	85	1747	1720	87	1752	1721	92	1758	1735	79	1743	1713	81	1749	1718	83
1496	1438	5	1516	1469	2	1478	1430	3	1515	1463	4	1504	1458	31	1500	1462	20
1426	1393	7	1457	1416	46	1431	1385	16	1448	1397	9	1432	1397	50	1427	1395	29
1400	1358	32	1420	1394	12	1401	1363	12	1414	1381	10	1400	1372	13	1406	1370	17
1397	1364	24	1376	1330	25	1390	1342	17	1368	1326	18	1384	1338	29	1395	1359	18
1347	1293	29	1337	1299	37	1343	1303	19	1326	1283	68	1335	1297	4	1335	1295	22
1232	1208	50	1297	1249	29	1254	1224	90	1242	1212	83	1282	1245	5	1248	1217	50
1208	1169	55	1193	1162	85	1190	1153	23	1171	1136	1	1198	1162	66	1206	1164	55
1093	1060	72	1071	1036	29	1101	1073	68	1123	1089	58	1105	1065	27	1099	1062	40
1053	1036	10	1032	998	59	1069	1042	17	1059	1031	41	1065	1044	22	1068	1050	19
1025	984	94	977	953	14	1026	990	59	1001	974	58	1028	990	53	1021	980	55
953	916	34	905	871	68	976	951	3	934	906	17	926	892	47	930	896	33
826	806	36	831	806	31	917	884	66	834	809	43	800	779	45	813	784	52
639	637	25	764	742	20	566	568	5	642	629	27	636	632	27	636	638	21
556	543	8	559	546	16	519	504	2	520	514	5	543	527	5	570	548	5
475	470	14	425	433	37	417	507	132	425	518	59	467	448	1	480	482	11
403	381	48	367	329	50	343	229	13	376	262	89	347	294	111	405	361	140
294	389	50	314	455	85	321	318	5	339	334	15	303	222	33	292	427	23
268	152	116	287	251	42	268	27	92	261	247	25	279	100	81	271	38	78
234	232	9	250	100	21	255	461	32	235	210	64	242	429	20	231	211	6
127	140	5	112	115	11	104	118	4	140	132	15	124	126	15	127	143	16
87	66	8	102	94	2	58	34	12	112	91	6	93	77	10	80	57	8

Table S11. Calculated harmonic (ν) and anharmonic (ν_{anh}) wavenumbers (cm^{-1}) and intensities (I , km mol^{-1}) for the deuterated conformers of HHA (**I**_{HHA-d}-**VI**_{HHA-d}).

I _{HHA-d}			II _{HHA-d}			III _{HHA-d}			IV _{HHA-d}			V _{HHA-d}			VI _{HHA-d}		
ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I	ν	ν_{anh}	I
3021	2857	52	3066	2925	26	3070	2934	28	3022	2895	39	3014	2920	45	3027	2872	49
3017	2902	35	2993	2860	63	2989	2836	58	2996	2850	65	3010	2807	47	2959	2845	61
2813	2713	39	2808	2702	40	2814	2715	41	2830	2729	40	2785	2685	41	2797	2698	45
2808	2702	39	2745	2642	41	2808	2702	40	2788	2682	39	2729	2622	5	2717	2611	4
2573	2478	10	2576	2484	4	2584	2490	6	2596	2499	4	2587	2497	12	2581	2493	9
1751	1719	84	1747	1711	88	1752	1721	90	1757	1730	81	1742	1712	81	1749	1721	83
1427	1397	22	1417	1388	9	1420	1388	10	1423	1395	12	1410	1378	28	1418	1387	24
1382	1347	3	1406	1367	12	1374	1341	18	1401	1364	6	1368	1328	6	1385	1352	7
1367	1325	5	1332	1302	2	1355	1321	9	1344	1309	11	1353	1319	3	1368	1327	5
1185	1143	67	1208	1176	40	1214	1169	20	1170	1133	26	1199	1160	16	1186	1146	70
1167	1136	29	1143	1101	29	1173	1143	9	1137	1112	20	1176	1142	74	1172	1139	23
1120	1094	19	1098	1070	7	1103	1078	64	1120	1092	55	1112	1083	7	1107	1080	15
1042	1015	3	1076	1048	12	1041	1018	12	1095	1070	24	1069	1038	18	1087	1054	27
1014	990	8	997	974	41	1026	992	2	1011	983	2	1016	986	12	1000	976	11
943	913	56	944	919	62	981	959	20	936	911	50	992	967	3	970	950	1
897	884	56	917	892	44	949	919	48	904	888	18	938	919	58	908	887	67
830	816	5	846	834	16	856	844	29	854	830	44	836	822	13	842	830	11
776	750	58	739	729	35	768	745	43	752	737	28	709	684	55	728	702	54
618	616	23	731	703	21	554	536	6	605	583	23	623	607	16	612	609	11
532	515	5	524	517	14	507	495	4	511	501	7	482	477	9	531	512	1
466	458	10	411	403	12	377	377	64	381	378	12	460	448	3	468	460	5
296	302	34	318	328	12	315	321	1	334	333	34	304	313	22	307	271	76
278	262	5	286	291	19	273	294	35	305	305	44	260	223	48	272	320	14
224	218	6	242	227	75	242	204	8	234	240	13	236	253	16	229	225	7
202	192	89	195	158	21	194	174	62	179	168	41	203	162	57	199	96	56
121	134	4	105	102	9	99	112	3	129	105	16	113	105	14	118	150	12
85	60	7	99	92	3	57	38	11	111	83	6	91	65	9	79	47	7

