

## Supplementary information: additional computational details

**Table S1** Equilibrium structures<sup>a</sup> of the keto isomers of *N*-hydroxyurea at the MP2/6-311++G(2d,2p) level of theory

Property	1Ea	1Eb	1Za	1Zb
r(C=O <sub>1</sub> )	1.2188	1.2191	1.2224	1.2111
r(C-N <sub>1</sub> )	1.3648	1.3726	1.3755	1.3870
r(C-N <sub>2</sub> )	1.4121	1.3983	1.3990	1.4118
r(N-O <sub>2</sub> )	1.4275	1.4122	1.4176	1.4138
r(N <sub>1</sub> -H <sub>1</sub> )	1.0032	1.0041	1.0051	1.0055
r(N <sub>1</sub> -H <sub>2</sub> )	1.0036	1.0047	1.0051	1.0057
r(N <sub>2</sub> -H <sub>3</sub> )	1.0104	1.0090	1.0107	1.0094
r(O <sub>2</sub> -H <sub>4</sub> )	0.9614	0.9660	0.9748	0.9607
r(H <sub>4</sub> ...O <sub>1</sub> )	-	-	1.9499	2.9556
r(H <sub>3</sub> ...O <sub>1</sub> )	2.4388	2.4607	-	-
r(H <sub>2</sub> ...O <sub>2</sub> )	2.1967	2.3231	-	-
φ(O <sub>1</sub> =C-N <sub>1</sub> )	125.55	125.15	124.96	124.62
φ(O <sub>1</sub> =C-N <sub>2</sub> )	119.56	120.62	121.73	124.04
φ(C-N <sub>2</sub> -O <sub>2</sub> )	113.94	117.44	111.76	112.98
φ(N <sub>1</sub> -C-N <sub>2</sub> )	114.66	114.22	113.30	111.31
φ(H <sub>1</sub> -N <sub>1</sub> -C)	114.60	113.85	113.45	112.55
φ(H <sub>2</sub> -N <sub>1</sub> -C)	117.56	117.36	116.62	116.85
φ(C-N <sub>2</sub> -H <sub>3</sub> )	109.40	112.86	112.42	112.91
φ(H <sub>3</sub> -N <sub>2</sub> -O <sub>2</sub> )	108.36	112.43	107.57	106.30
φ(N <sub>2</sub> -O <sub>2</sub> -H <sub>4</sub> )	102.63	106.26	101.94	103.34
φ(H <sub>1</sub> -N <sub>1</sub> -H <sub>2</sub> )	118.05	116.92	114.79	113.84
φ(C=O <sub>1</sub> ...H <sub>3</sub> )	54.29	54.64	-	-
φ(C=O <sub>1</sub> ...H <sub>4</sub> )	-	-	82.71	69.58
φ(N <sub>1</sub> -H <sub>2</sub> ...O <sub>1</sub> )	103.86	97.32	-	-
φ(O-H <sub>4</sub> ...O <sub>1</sub> )	-	-	120.74	64.89
θ(O <sub>1</sub> CN <sub>2</sub> H <sub>3</sub> )	37.51	-27.88	-129.15	-142.09
θ(O <sub>1</sub> CN <sub>2</sub> O <sub>2</sub> )	158.9	-161.16	-8.07	-21.41
θ(N <sub>1</sub> CN <sub>2</sub> O <sub>2</sub> )	-26.26	19.32	171.71	160.07
θ(CN <sub>2</sub> O <sub>2</sub> H <sub>4</sub> )	123.60	63.52	-1.66	98.52
θ(H <sub>3</sub> N <sub>2</sub> O <sub>2</sub> H <sub>4</sub> )	-114.37	-69.96	122.20	-137.11
θ(N <sub>1</sub> CN <sub>2</sub> H <sub>3</sub> )	-147.71	152.60	50.62	39.40
θ(H <sub>1</sub> N <sub>1</sub> CO <sub>1</sub> )	-14.16	-16.79	-13.20	-16.11
θ(H <sub>2</sub> N <sub>1</sub> CO <sub>1</sub> )	-159.45	-158.62	-149.98	-150.60
θ(H <sub>1</sub> N <sub>1</sub> CN <sub>2</sub> )	171.43	162.70	167.03	162.40
θ(H <sub>2</sub> N <sub>1</sub> CN <sub>2</sub> )	26.14	20.87	30.25	27.91
μ	3.449	2.958	3.515	3.745

<sup>a</sup> see Figure 1 for atom numbering; the bond distances are given in Å, the angles in degrees, dipole moments in Debyes.

**Table S2** Relative energies ( $\Delta E$ ), relative zero-point corrected energies ( $\Delta E_{ZPE}$ ) (in  $\text{kJ mol}^{-1}$ ), dipole moments ( $\mu$  /D) and abundances at 298 K for *N*-hydroxyurea isomers calculated at the MP2/6-311++G(2d,2p) level in water solution (C-PCM calculations)

isomer	$\Delta E$	$\Delta E_{ZPE}$	$\mu$	% <sub>298</sub>
<b>1Ea</b>	0.00	0.00	5.46	87.2
<b>1Za</b>	12.07	11.88	6.37	1.2
<b>1Eb</b>	5.54	5.52	5.22	8.6
<b>1Zb</b>	8.77	8.73	6.50	3.0

**Table S3** Selected geometric parameters calculated at the MP2/6-311++G(2d,2p) level for the keto isomers of *N*-hydroxyurea in water (C-PCM calculations)

Parameter <sup>a</sup>	1Ea	1Eb	1Za	1Zb
r(C=O <sub>1</sub> )	1.237	1.237	1.230	1.229
r(C-N <sub>1</sub> )	1.348	1.351	1.366	1.366
r(C-N <sub>2</sub> )	1.397	1.390	1.392	1.395
r(N-O <sub>2</sub> )	1.420	1.411	1.404	1.411
r(N <sub>2</sub> -H <sub>3</sub> )	1.024	1.023	1.024	1.024
r(O <sub>2</sub> -H <sub>4</sub> )	0.981	0.985	0.984	0.979
$\phi$ (C-N <sub>2</sub> -H <sub>3</sub> )	111.1	113.3	115.2	114.6
$\phi$ (H <sub>3</sub> -N <sub>2</sub> -O <sub>2</sub> )	109.1	112.1	111.04	108.5
$\phi$ (N <sub>2</sub> -O <sub>2</sub> -H <sub>4</sub> )	103.6	106.2	106.3	103.8
$\theta$ (O <sub>1</sub> CN <sub>2</sub> H <sub>3</sub> )	37.6	-33.2	-146.0	-150.8
$\theta$ (O <sub>1</sub> CN <sub>2</sub> O <sub>2</sub> )	161.6	-165.8	-14.4	-25.0
$\theta$ (CN <sub>2</sub> O <sub>2</sub> H <sub>4</sub> )	119.8	72.5	-58.6	108.9
$\theta$ (H <sub>3</sub> N <sub>2</sub> O <sub>2</sub> H <sub>4</sub> )	-115.1	-60.7	74.9	-122.2
$\mu$	5.46	5.22	6.37	6.50

<sup>a</sup> see Figure 1 for atom numbering; the bond distances are given in Å, the angles in degrees, dipole moments in Debyes.

**Table S4** Definition of internal coordinates used in the normal mode analysis of the 1*Ea* and 1*Za* isomers of *N*-hydroxyurea

1 <i>Ea</i>		1 <i>Za</i>	
definition <sup>a</sup>	vibration <sup>b</sup>	definition <sup>a</sup>	vibration <sup>b</sup>
$\nu_1$	$\nu \text{ C}=\text{O}_1$	$\nu_1$	$\nu \text{ C}=\text{O}_1$
$\nu_2$	$\nu \text{ C}-\text{N}_1 + \nu \text{ C}-\text{N}_2$	$\nu_2$	$\nu \text{ C}-\text{N}_1 + \nu \text{ C}-\text{N}_2$
$\nu_3$	$\nu \text{ C}-\text{N}_1 - \nu \text{ C}-\text{N}_2$	$\nu_3$	$\nu \text{ C}-\text{N}_1 - \nu \text{ C}-\text{N}_2$
$\nu_4$	$\nu \text{ N}-\text{O}_2$	$\nu_4$	$\nu \text{ N}-\text{O}_2$
$\nu_5$	$\nu \text{ N}_2-\text{H}_3$	$\nu_5$	$\nu \text{ N}_2-\text{H}_3$
$\nu_6$	$\nu \text{ O}_2-\text{H}_4$	$\nu_6$	$\nu \text{ O}_2-\text{H}_4$
$\nu_7$	$\nu \text{ N}_1-\text{H}_1 + \nu \text{ N}_1-\text{H}_2$	$\nu_7$	$\nu \text{ N}_1-\text{H}_1 + \nu \text{ N}_1-\text{H}_2$
$\nu_8$	$\nu \text{ N}_1-\text{H}_1 - \nu \text{ N}_1-\text{H}_2$	$\nu_8$	$\nu \text{ N}_1-\text{H}_1 - \nu \text{ N}_1-\text{H}_2$
$\delta_1$	$2\delta \text{ O}_1=\text{C}-\text{N}_1 - \delta \text{ O}_1=\text{C}-\text{N}_2 - \delta \text{ N}_1-\text{C}-\text{N}_2$	$\delta_1$	$2\delta \text{ N}_1-\text{C}-\text{N}_2 - \delta \text{ O}_1=\text{C}-\text{N}_1 - \delta \text{ O}_1=\text{C}-\text{N}_2$
$\delta_2$	$\delta \text{ O}_1=\text{C}-\text{N}_2 - \delta \text{ N}_1-\text{C}-\text{N}_2$	$\delta_2$	$\delta \text{ O}_1=\text{C}-\text{N}_2 - \delta \text{ O}_1=\text{C}-\text{N}_1$
$\delta_3$	$2\delta \text{ C}-\text{N}_2-\text{O}_2 - \delta \text{ C}-\text{N}_2-\text{H}_3 - \delta \text{ H}_3-\text{N}_2-\text{O}_2$	$\delta_3$	$2\delta \text{ C}-\text{N}_2-\text{O}_2 - \delta \text{ C}-\text{N}_2-\text{H}_3 - \delta \text{ H}_3-\text{N}_2-\text{O}_2$
$\delta_4$	$\delta \text{ C}-\text{N}_2-\text{H}_3 - \delta \text{ H}_3-\text{N}_2-\text{O}_2$	$\delta_4$	$\delta \text{ C}-\text{N}_2-\text{H}_3 - \delta \text{ H}_3-\text{N}_2-\text{O}_2$
$\delta_5$	$\delta \text{ N}_2-\text{O}_2-\text{H}_4$	$\delta_5$	$\delta \text{ N}_2-\text{O}_2-\text{H}_4$
$\delta_6$	$2\delta \text{ H}_1-\text{N}_1-\text{H}_2 - \delta \text{ C}-\text{N}_1-\text{H}_1 - \delta \text{ C}-\text{N}_1-\text{H}_2$	$\delta_6$	$2\delta \text{ H}_1-\text{N}_1-\text{H}_2 - \delta \text{ C}-\text{N}_1-\text{H}_1 - \delta \text{ C}-\text{N}_1-\text{H}_2$
$\delta_7$	$\delta \text{ C}-\text{N}_1-\text{H}_1 - \delta \text{ C}-\text{N}_1-\text{H}_2$	$\delta_7$	$\delta \text{ C}-\text{N}_1-\text{H}_1 - \delta \text{ C}-\text{N}_1-\text{H}_2$
$\gamma_1$	$\gamma \text{ N}_1-\text{C}(=\text{O}_1)-\text{N}_2$	$\gamma_1$	$\gamma \text{ N}_1-\text{C}(=\text{O}_1)-\text{N}_2$
$\gamma_2$	$\gamma \text{ C}-\text{N}_2 (-\text{H}_3)-\text{O}_2$	$\gamma_2$	$\gamma \text{ C}-\text{N}_2 (-\text{H}_3)-\text{O}_2$
$\gamma_3$	$\gamma \text{ C}-\text{N}_1 (-\text{H}_1)-\text{H}_2$	$\gamma_3$	$\gamma \text{ C}-\text{N}_1 (-\text{H}_1)-\text{H}_2$
$\tau_1$	$\tau \text{ C}-\text{N}_2-\text{O}_2-\text{H}_4 + \tau \text{ H}_3-\text{N}_2-\text{O}_2-\text{H}_4$	$\tau_1$	$\tau \text{ C}-\text{N}_2-\text{O}_2-\text{H}_4 + \tau \text{ H}_3-\text{N}_2-\text{O}_2-\text{H}_4$
$\tau_2$	$\tau \text{ O}_1=\text{C}-\text{N}_2-\text{O}_2 + \tau \text{ N}_1-\text{C}-\text{N}_2-\text{O}_2 +$ $\tau \text{ O}_1=\text{C}-\text{N}_2-\text{H}_3 + \tau \text{ N}_1-\text{C}-\text{N}_2-\text{H}_3$	$\tau_2$	$\tau \text{ O}_1=\text{C}-\text{N}_2-\text{O}_2 + \tau \text{ N}_1-\text{C}-\text{N}_2-\text{O}_2 +$ $\tau \text{ O}_1=\text{C}-\text{N}_2-\text{H}_3 + \tau \text{ N}_1-\text{C}-\text{N}_2-\text{H}_3$
$\tau_3$	$\tau \text{ O}_1=\text{C}-\text{N}_1-\text{H}_1 + \tau \text{ N}_1-\text{C}-\text{N}_2-\text{H}_1 +$ $\tau \text{ O}_1=\text{C}-\text{N}_1-\text{H}_2 + \tau \text{ N}_1-\text{C}-\text{N}_2-\text{H}_2$	$\tau_3$	$\tau \text{ O}_1=\text{C}-\text{N}_1-\text{H}_1 + \tau \text{ N}_1-\text{C}-\text{N}_2-\text{H}_1 +$ $\tau \text{ O}_1=\text{C}-\text{N}_1-\text{H}_2 + \tau \text{ N}_1-\text{C}-\text{N}_2-\text{H}_2$

<sup>a</sup> $\nu$ ,  $\delta$ ,  $\gamma$ , and  $\tau$  denote stretching, in-plane bending, out-of-plane bending, and torsion vibrations, respectively. <sup>b</sup>see Figure 1 for atom numbering.

**Table S5** Potential energy distribution calculated for the 1Ea isomer of *N*-hydroxyurea and its deuterated analogue

1Ea - NH <sub>2</sub> CONHOH		ND <sub>2</sub> CONDOD		PED <sup>c,d</sup> (%)
calc	exp	calc	exp	
3841 (75) <sup>a</sup>	3590.4 (0.10) <sup>b</sup>	2799 (37) <sup>a</sup>	2669.3 (0.06) <sup>b</sup>	vOH (100) {vOD (100)}
3762 (82)	3556.7 (0.13)	2785 (50)	2655.7 (0.15)	v <sub>as</sub> NH <sub>2</sub> (99) {v <sub>as</sub> ND <sub>2</sub> (99)}
3629 (46)	3440.5 (0.06)	2620 (44)	2506.5 (0.07)	v <sub>s</sub> NH <sub>2</sub> (99) {v <sub>s</sub> ND <sub>2</sub> (98)}
3600 (39)	3383.5 (0.05)	2636 (22)	2581.5 (0.02)	vNH (100) {vND (99)}
1788 (420)	1744.0 (1.00)	1773 (417)	1733.0 (1.00)	vC=O (67), v <sub>s</sub> NCN (12) {vC=O (73), v <sub>s</sub> NCN (11)}
1614 (121)	1567.0 (0.17)	1208 (8)		δNH <sub>2</sub> (83) {δND <sub>2</sub> (49), v <sub>s</sub> NCN (20), δND (11), vNO (10)}
1447 (49)	1405.0 (0.13)	1116 (3)		δNH (51), δOH (20) {δND (40), δND <sub>2</sub> (23), vNO (18)}
1428 (132)	1384.0 (0.12)	1422 (301)	1379.5 (0.26)	v <sub>as</sub> NCN (40), δNH (32) {v <sub>as</sub> NCN (68), δOCN (13)}
1384 (56)	1347.3 (0.05)	1042 (12)	1008.8 (0.04)	δOH (67) {δOD (60), δND (28)}
1129 (7)	1063.0 (0.003)	932 (4)		ρNH <sub>2</sub> (56) {ρND <sub>2</sub> (48), v <sub>s</sub> NCN (14), vNO (10)}
1058 (32)	1025.7 (0.06)	978 (58)	957.6 (0.09)	vNO (61), δOH (10) {vNO (41), δOD (35)}
976 (41)	949.1 (0.03)	867 (8)	846.7 (0.01)	v <sub>s</sub> NCN (52), δCNO (20), γNH (18) {v <sub>s</sub> NCN (38), δCNO (16), γNCN (14), γND (10)}
795 (76)	763.4 (0.08)	774 (39)	739.3 (0.06)	γNCN (48), γNH (17), v <sub>s</sub> NCN (14) {γNCN (62), γND (11), v <sub>s</sub> NCN (10)}
684 (161)	636.6 (0.24)	576 (74)		γNH (30), δCNO (14), v <sub>s</sub> NCN (13), γNCN (12), vNO (10) {γND (30), δCNO (25), v <sub>s</sub> NCN (18), vNO (11)}
595 (46)	604.9 (0.13)	408 (14)		τNH <sub>2</sub> (32), δNCN (23), γOH (18) {τND <sub>2</sub> (75)}
543 (18)	554.9 (0.07)	489 (0)		δOCN (45), τNH <sub>2</sub> (21), δNCN (16) {δOCN (55), ρND <sub>2</sub> (23)}
529 (14)	525.8 (0.03)	518 (66)		δNCN (56), δOCN (26) {δNCN (40), γND (32)}
488 (254)		370 (146)		ωNH <sub>2</sub> (72), v <sub>as</sub> NCN (11) {ωND <sub>2</sub> (82)}
383 (16)		284 (10)		γOH (44), ωNH <sub>2</sub> (20) {γOD (50), ωND <sub>2</sub> (16), τND <sub>2</sub> (10)}
320 (9)		300 (7)		δCNO (41), δNCN (27), γNH (14) {δCNO (32), δNCN (28), γND (13)}
184 (2)		171 (2)		γOCNO (80) {γOCNO (81)}

<sup>a</sup> The MP2/6-311++G(2d,2p) calculated harmonic frequencies (in cm<sup>-1</sup>) and intensities (in km mol<sup>-1</sup>) are given. <sup>b</sup> For the observed bands the relative integrated intensities are given in parentheses. <sup>c</sup> All values less than 10% have been omitted. Definition of internal coordinates is given in Table S2 (ESI<sup>†</sup>). <sup>d</sup> The assignment obtained for the ND<sub>2</sub>CONDOD molecule is given in braces.

**Table S6** Potential energy distribution calculated for the 1Za isomer of *N*-hydroxyurea

1Za - NH <sub>2</sub> CONHOH		PED <sup>c</sup> (%)
calculated	experimntl	
3625 (99) <sup>a</sup>	3398.0 (0.44) <sup>b</sup>	vOH (97)
3736 (59)	3535.0 (0.28)	v <sub>as</sub> NH <sub>2</sub> (100)
3616 (52)	3430.1 (0.18)	v <sub>s</sub> NH <sub>2</sub> (99)
3587 (26)	3372.5 (0.22)	vNH (97)
1777 (286)	1725.4 (0.74)	vC=O (68), v <sub>s</sub> NCN (12)
1636 (85)		δNH <sub>2</sub> (88)
1533 (28)		δNH (48), δOH (22), v <sub>as</sub> NCN (10)
1354 (48)	1323.5 (0.31)	v <sub>as</sub> NCN (48), δNH (25)
1435 (302)	1394.0 (1.00)	δOH (39), v <sub>as</sub> NCN (28), δNH (19)
1134 (6)		ρNH <sub>2</sub> (48), vNO (25)
1089 (25)		vNO (51), v <sub>s</sub> NCN (27)
997 (39)	954.5 (0.33)	v <sub>s</sub> NCN (38), δCNO (25), γNH (22)
785 (81)	692.9 (0.15)	γNCN (43), γNH (23), v <sub>s</sub> NCN (20)
643 (120)	535.2 (0.39)	γNH (38), ωNH <sub>2</sub> (23), δNCN (11)
418 (30)		τNH <sub>2</sub> (56), γOH (25)
705 (86)	680.5 (0.58)	δOCN (24), v <sub>s</sub> NCN (20), δNCN (19), γNH (15)
472 (40)		δNCN (43), δOCN (19), ρNH <sub>2</sub> (11)
522 (175)		ωNH <sub>2</sub> (36), γNH (24)
429 (110)		γOH (61), τNH <sub>2</sub> (22)
313 (32)		δCNO (38), δOCN (29)
178 (12)		γOCNO (61), γOH (27)

<sup>a</sup> The MP2/6-311++G(2d,2p) calculated harmonic frequencies (in cm<sup>-1</sup>) and intensities (in km mol<sup>-1</sup>) are given. <sup>b</sup> For the observed bands the relative integrated intensities are given in parentheses. <sup>c</sup> All values less than 10% have been omitted. Definition of internal coordinates is given in Table S2 (ESI†).