

SUPPORTING INFORMATION by Cai and Reimers on pyrimidine-water

Table S1: The calculated vibrational frequency shifts of the normal modes of pyrimidine and water (cm^{-1}) arising from the formation of ground-state $\text{H}_2\text{O}:\text{pyrimidine}$ and $2\text{H}_2\text{O}:\text{pyrimidine}$ complexes.

Type ^a	Vibration	$\text{H}_2\text{O}:\text{pyrimidine}$				$2\text{H}_2\text{O}:\text{pyrimidine}$	
		Calculated			Observed	Calculated	
		B3LYP	CASSCF	CCSD	shift from argon matrix ^b	B3LYP	CASSCF
O-H		-37	-14	-40		-25	-11
O-H		-212	48	-116	-201	-185	50
CH	2	5	3	4	4	4	2
CH	7b	3	0	6	-1	-3	15
CH	13	13	6	7	8	14	0
CC	20a	6	5	7	5	5	5
H-O-H		39	67	39	24	42	44
CC	8a	7	5	6	6	11	4
CC	8b	-2	-1	1	0	-2	-3
CC	19b	1	1	1	0	5	3
CC	19a	4	4	6	4	12	10
CC	14	6	2	2	6	12	7
H	3	1	3	1	3	1	8
H	9a	0	3	4	2	8	4
H	15	3	0	3	0	2	-1
H	18b	3	-2	3	1	3	0
C	12	0	2	2	0	2	4
CC	1	9	4	7		10	4
H \perp	5	3	2	6		26	21
H \perp	17b	8	2	2	6	1	3
H \perp	17a	0	4	14		15	11
H \perp	10b	4	9	2	3	12	16
C \perp	4	-1	1	-4	3	5	4
C	6b	5	3	5	4	8	4
C	6a	4	2	5	4	5	3
C \perp	16b	-2	3	0	-3	6	2
C \perp	16a	displace	missing	-10		3	-1

a: CC: ring stretch, CH: hydrogen stretch, C||: in-plane ring bend, H||: in-plane hydrogen bend, C \perp : out of plane ring bend, H \perp : out of plane hydrogen bend. See \R{ibr67} for more details. *b:* observed shifts with respect to corresponding experimental values of monomer H_2O and pyridine in Ar matrix, respectively.

Table S2: The calculated vibrational frequency shifts of the normal modes of pyrimidine and water (cm^{-1}) arising from the formation of excited-state $\text{H}_2\text{O}:\text{pyrimidine}$ and $2\text{H}_2\text{O}:\text{pyrimidine}$ complexes.

Type ^a	Vibration	$\text{H}_2\text{O}:\text{pyrimidine}$			$2\text{H}_2\text{O}:\text{pyrimidine}$	
		Calculated			Calculated	
		TD-B3LYP	CASSCF	EOM-CCSD	TD-B3LYP	CASSCF
O-H		17	-18	-43	-125	-12
O-H		-371	46	-113	-396	55
CH	2	44	15	19	28	16
CH	7b	25	-6	21	-36	-1
CH	13	-53	-15	-38	-31	-20
CC	20a	-68	4	-2	-243	5
H-O-H		40	78	32	36	77
CC	8a	211	-9	74	195	-7
CC	19a	24	38	45	49	44
CC	8b	85	-3	4	86	0
CC	19b	-11	8	-4	-8	10
CC	14	19	79	-25	20	82
H \parallel	3	-24	38	-10	-54	41
H \parallel	9a	16	14	9	-13	21
H \parallel	15	-24	35	14	10	32
H \parallel	18b	-20	22	-23	38	20
C \parallel	12	-6	9	-21	-24	10
CC	1	-15	-2	7	0	-2
H \perp	5	-45	4	-55	-10	3
H \perp	17b	-96	10	-24	-113	14
H \perp	17a	-32	-31	-53	-29	11
H \perp	10b	72	46	153	46	-2
C \perp	4	-36	36	-33	-24	67
C \parallel	6b	-	-		-	-
C \parallel	6a	23	58	-10	-16	69
C \perp	16b	-4	-142	-48	46	76
C \perp	16a	-132	-69		-64	-27

a: CC: ring stretch, CH: hydrogen stretch, C \parallel : in-plane ring bend, H \parallel : in-plane hydrogen bend, C \perp : out of plane ring bend, H \perp : out of plane hydrogen bend. See \R{ibr67} for more details.

b: observed shifts with respect to corresponding experimental values of monomer H_2O and pyridine in Ar matrix, respectively.

Table S3: Calculated intermolecular vibrational frequencies (in cm^{-1}) of the electronic states of the $\text{H}_2\text{O}:\text{pyrimidine}$ complex in its ground state and lowest (n,π^*) excited states

Type	GS			(n,π^*)		
	B3LYP	CASSCF	CCSD	TD-B3LYP	CASSCF	EOM-CCSD
$\nu(\text{H}_2\text{O})$	613	532	552	603	550	473
$\nu(\text{H}_2\text{O})$	423	371	397	340	355	364
$\nu(\text{OH-N})$	146	124	146	194	116	132
$\tau(\text{OH-N})$	53	49	33	13	36	36i
$\gamma(\text{OH-N})$	39	37	34	54	32	27
$\beta(\text{OH-N})$	45i	-	77i	179i	92i	123i

Table S4: Calculated intermolecular vibrational frequencies (in cm^{-1}) of the electronic states of the $2\text{H}_2\text{O}:\text{pyrimidine}$ complex in its ground state and lowest (n,π^*) excited states (values in parentheses are for second H_2O)

Type	GS		(n,π^*)	
	B3LYP	CASSCF	TD-B3LYP	CASSCF
$\nu(\text{H}_2\text{O})$	573 (564)	513 (505)	693 (578)	501 (496)
$\nu(\text{H}_2\text{O})$	397 (213)	341 (183)	382 (194)	329 (178)
$\nu(\text{OH-N})$	163 (97)	134 (76)	103 (67)	133 (62)
$\tau(\text{OH-N})$	78	64	67	56
$\gamma(\text{OH-N})$	60 (44)	58 (44)	51 (134)	44 (33)
$\beta(\text{OH-N})$	87i (232i)	35 (155i)	37i (211i)	53i (180i)