

Electronic Supplementary Information (ESI)

for

**Sequential Microhydration of Cationic 5-Hydroxyindole (5HI⁺):
Infrared Photodissociation Spectra of 5HI⁺-W_n Clusters (W=H₂O, n≤4)**

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Table S1. Selected bond lengths (Å), vibrational frequencies (cm^{-1}), and dissociation energies (cm^{-1}) of $\text{a5HI}^{(+)}$ and $\text{a5HI}^{(+)}\text{-W}_n\text{-L}_m$ clusters calculated at the B3LYP-D3/aug-cc-pVTZ level.^a

Species	ΔE_0	D_0	ν_{NH}	ν_{OH}	r_{NH}	r_{OH}	R^b
a5HI-W(OH)	0	1703	3519 (60)	3484 (666)	1.0024	0.9704	1.891
a5HI-W(NH)	109	1594	3398 (566)	3656 (52)	1.0095	0.9616	1.982
a5HI-W(π)	289	1305	3513 (79)	3655 (60)	1.0030	0.9618	3.408
a5HI ⁺ -W(OH)	157	5463	3457 (169)	2993 (2389)	1.0082	0.9990	1.645
a5HI ⁺ -W(NH)	1215	4405	3123 (1315)	3587 (237)	1.0275	0.9676	1.783
a5HI ⁺ -W(π)	3543	2076	3458 (179)	3584 (228)	1.0082	0.9680	3.114
a5HI ⁺ -W(OH)-Ar(NH)	158	6017	3440 (390)	3001 (2436)	1.0093	0.9985	1.648 W / 2.565 (Ar)
a5HI ⁺ -W(OH)-Ar(π)	193	5982	3458 (165)	2997 (2367)	1.0081	0.9987	1.647 W / 3.515 (Ar)
a5HI ⁺ -W(NH)-Ar(OH)	1066	5108	3126 (1077)	3588 (233)	1.0270	0.9694	1.786 W / 2.489 (Ar)
a5HI ⁺ -W(NH)-Ar(π)	1216	4958	3133 (994)	3549 (534)	1.0273	0.9676	1.784 W / 3.545 (Ar)
a5HI ⁺ -W(OH)-N ₂ (NH)	152	6421	3398 (586)	3009 (2441)	1.0113	0.9980	1.650 W / 2.193 (N ₂)
a5HI ⁺ -W(OH)-N ₂ (W)	252	6321	3459 (171)	2892 (2862)	1.0081	1.0046	1.611 W / 2.091 (N ₂)
a5HI ⁺ -W(NH)-N ₂ (OH)	933	5640	3136 (1388)	3466 (1009)	1.0267	0.9734	1.787 W / 2.021 (N ₂)
a5HI ⁺ -W(NH)-N ₂ (W)	1410	5163	3074 (1732)	3588 (216)	1.0304	0.9676	1.755 W / 2.138 (N ₂)
a5HI ⁺ -W ₂ (OH/NH)	147	9493	3166 (1124)	3049 (2426)	1.0248	0.9955	1.665 (OH) / 1.802 (NH)
a5HI ⁺ -W ₂ (OH/W)	335	9304	3461 (164)	2649 (3655)	1.0078	1.0185	1.547
a5HI ⁺ -W ₂ (NH/W)	1820	7819	2940 (2328)	3592 (229)	1.0383	0.9673	1.693
a5HI ⁺ -W ₃ (OH/W/NH)	76	13174	3185 (1260)	2735 (3622)	1.0235	1.0132	1.568 (OH) / 1.813 (NH)
a5HI ⁺ -W ₃ (OH/NH/W)	531	12719	3005 (2742)	3081 (1597)	1.0340	0.9939	1.675 (OH) / 1.719 (NH)
a5HI ⁺ -W ₃ (OH/W/W)	532	12717	2194 (4828)	3466 (156)	1.0074	1.0474	1.452
a5HI ⁺ -W ₃ (NH/W/W)	2518	10732	2735 (3027)	3594 (222)	1.0509	0.9670	1.622

^a IR intensities (km/mol) are listed in parentheses. Corresponding values for $\text{s5HI}^{(+)}$ -W are available in Table 1. The bold entries mark the most stable isomer of a given species.

^b Intermolecular bond lengths. The lengths of the π -bonds are distances to the aromatic plane.

Table S2. Minima of the reduced gradient $s(\rho) \sim |\text{grad}(\rho)|/\rho^{4/3}$ (in a.u.) as a function of the oriented electron density ρ^* (only negative) accounting for the attractive noncovalent interaction (NCI) in a5HI-W and $\text{a5HI}^{+}\text{-W}$.

Cluster	XH...W	CH...W	π ...W
a5HI-W(OH)	-0.0288	-0.0050	
a5HI-W(NH)	-0.0228	-0.0014	
a5HI-W(π)			-0.0083
a5HI ⁺ -W(OH)	-0.0518	-0.0072	
a5HI ⁺ -W(NH)	-0.0373	-0.0023	
a5HI ⁺ -W(π)			-0.0088

Figure S1. Structures of $a5\text{HI}^+-\text{W}_n$ ($n=1-3$) calculated at the B3LYP-D3/aug-cc-pVTZ level (Table S1). Bond lengths are given in Å.

Figure S2. Structures of $a5\text{HI}^+-\text{W-Ar}$ and $a5\text{HI}^+-\text{W-N}_2$ calculated at the B3LYP-D3/aug-cc-pVTZ level (Table S1). Bond lengths are given in Å.

Figure S3. Comparison of the IRPD spectra of $5\text{HI}^+-\text{W}$ generated by electron ionization (EI-IR) and by REMPI via the corresponding S_1 origins of $s/a5\text{HI}^+-\text{W(OH)}$ and $s/a5\text{HI}^+-\text{W(NH)}$ (REMPI-IR).

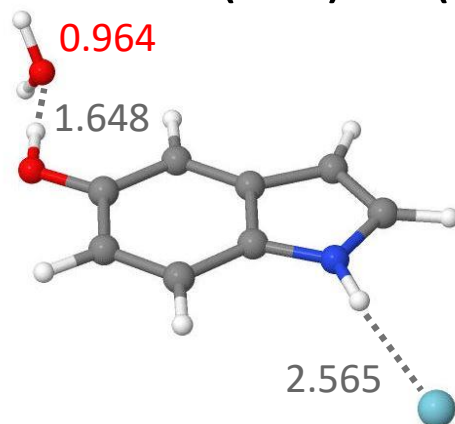
Figure S4. Noncovalent (NCI) interactions in $s\text{-HI}^{(+)}-\text{W}$ visualized via the reduced electron density gradient $s(\rho) \sim |\text{grad}(\rho)|/\rho^{4/3}$ as a function of the oriented electron density $\rho^* = \rho \text{sign}(\lambda_2)$ (Table 4). BGR color coding ($-1.25 < \rho^* < 1.25$ a.u.) is used for the isosurfaces (isosurface value of 0.5 a.u.); blue: attractive interactions (negative λ_2); red: repulsive interactions (positive λ_2); green: weak van der Waals contact (λ_2 close to zero). The reader is referred to refs 59 and 60 for detailed information on the NCI technique.

Figure S5. Noncovalent interactions in $a\text{-HI}^{(+)}-\text{W}$ visualized via the reduced electron density gradient $s(\rho) \sim |\text{grad}(\rho)|/\rho^{4/3}$ as a function of the oriented electron density $\rho^* = \rho \text{sign}(\lambda_2)$ (Table S2). BGR color coding ($-1.25 < \rho^* < 1.25$ a.u.) is used for the isosurfaces (isosurface value of 0.5 a.u.); blue: attractive interactions (negative λ_2); red: repulsive interactions (positive λ_2); green: weak van der Waals contact (λ_2 close to zero). The reader is referred to refs 59 and 60 for detailed information on the NCI technique.

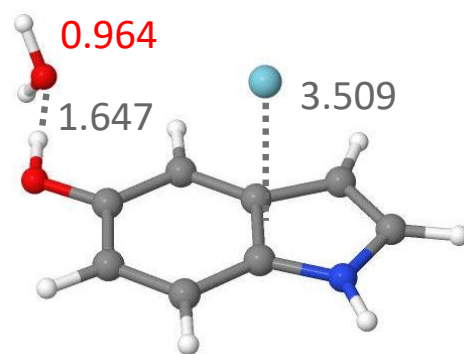


ORTEP diagram of the molecular structure of 2,2,2-trifluoroethyl 4-(2,2,2-trifluoroethyl)phenylcarbamate. The structure shows a biphenyl-like core with trifluoroethyl groups. Bond lengths are labeled: 0.963 Å (C-O), 1.768 Å (C-C), 0.979 Å (C-O), 1.767 Å (C-C), and 1.452 Å (C-N).

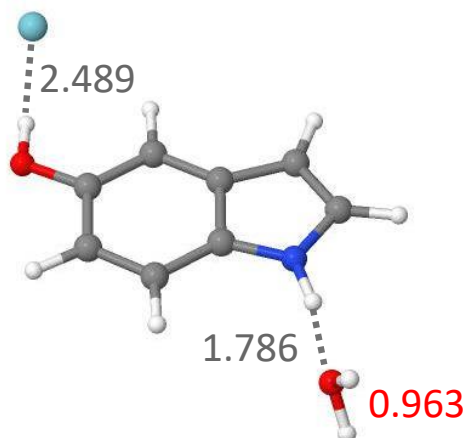
a5HI⁺-W(OH)-Ar(NH)



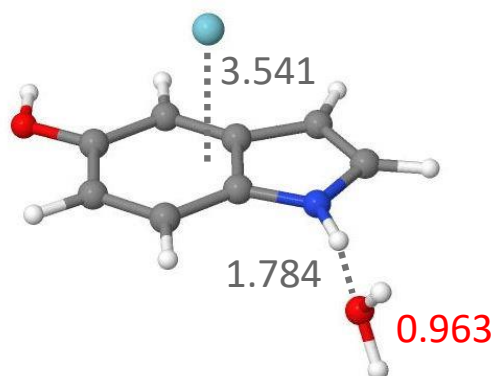
a5HI⁺-W(OH)-Ar(π)



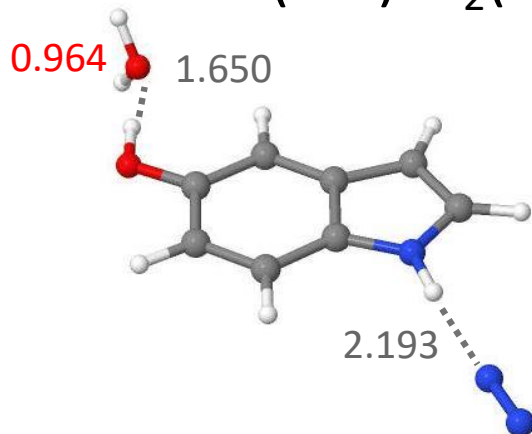
a5HI⁺-W(NH)-Ar(OH)



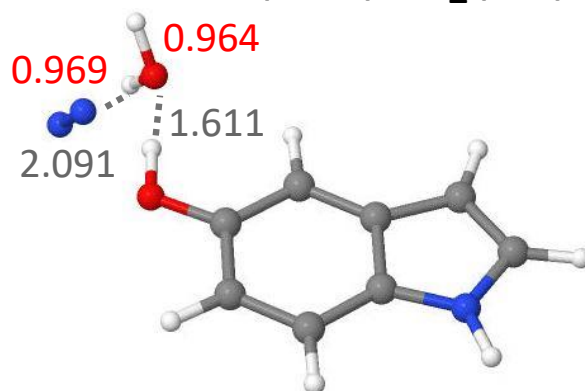
a5HI⁺-W(NH)-Ar(π)



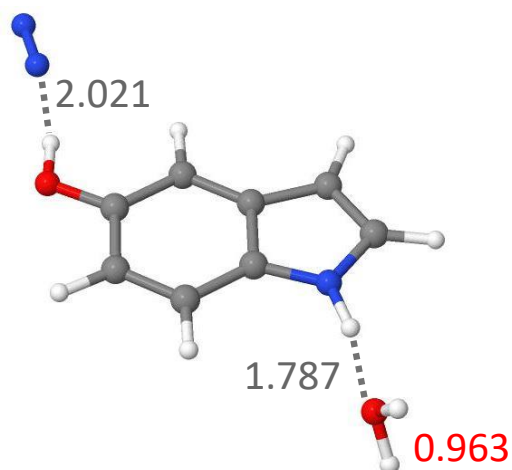
a5HI⁺-W(OH)-N₂(NH)



a5HI⁺-W(OH)-N₂(W)



a5HI⁺-W(NH)-N₂(OH)



a5HI⁺-W(NH)-N₂(W)

