

TABLE S1. Peak Frequencies and Assignments for Raman Spectra of Neat and Adsorbed Benzene.

Raman Spectral Bands (cm ⁻¹)				
Neat Benzene	Benzene on SiO ₂ (hy) ^c	Benzene on SiO ₂ (dehy) ^c	Assignment ^{a,b}	Wilson Notation
607			α (CCC)	6a,6b
850			γ (CH)	10a,10b
993	991	991	ν_{ring}	1
1178	1176	1176	δ (CH)	9a,9b
1588	1585	1585	$\nu(\text{CC})_{\text{ring}}$	8b
1607	1607	1606	$\nu(\text{CC})_{\text{ring}}$	8a
2948	2952	2954	comb.	
3061	3070	3070	$\nu(\text{CH})_{\text{ring}}$	7a,7b
3166			comb.	
3186	3188		comb.	

^a From References 45-47.

^b α = backbone deformation; γ = deformation; ν = stretch; δ = bend

^c (hy) = hydrated, (dehy) = dehydrated

TABLE S2. Peak Frequencies and Assignments for Raman Spectra of Neat and Adsorbed Toluene.

Raman Spectral Bands (cm ⁻¹)				
Neat Toluene	Toluene on SiO ₂ (hy) ^c	Toluene on SiO ₂ (dehy) ^c	Assignment ^{a,b}	Wilson Notation
521			ring (X sens.)	6a
622			α(CCC)	6b
786	785	785	v _{ring}	1
1003	1003	1003	v _{ring} (X sens.)	12
1030	1030	1029	δ(CH)	18a
1156			δ(CH)	9b
1179			δ(CH)	9a
1210	1211	1210	v _{ring} (X sens.)	13
1380	1384	1384	δ(CH ₃)	
1586	1585	1586	v(CC) _{ring}	8b
1605	1605	1605	v(CC) _{ring}	8a
2736			comb.	
2869	2877	2878	v _s (CH ₃)	
2919	2929	2929	v _s (CH ₃) _{FR}	
2982	2983	2983	comb.	
3003		3005	v(CH) _{ring}	
3055	3062	3061	v(CH) _{ring}	2
3170			comb.	
3206			comb.	

^a From References 45, 50.

^b α = backbone deformation; v = stretch; δ = bend

^c (hy) = hydrated, (dehy) = dehydrated

TABLE S3. Peak Frequencies and Assignments for Raman Spectra of Neat and Adsorbed 4-Picoline.

Neat 4-Picoline	Raman Spectral Bands (cm ⁻¹)				Wilson Notation	
	0.1 M Aqueous 4-Picoline	4-Picoline on SiO ₂ (hy) ^c	4-Picoline on SiO ₂ (dehy) ^c	1.0 M Aqueous pH<3		
516	526	530	527	521	ring (X sens.)	6a
671	669	667	667	653	α(CCC)	6b
803	809	807	806	808	ring (X sens.)	12
995	1009	1017	1015	1013	v _{ring}	1
1069	1071	1069	1070	1066	δ(CH)	18a
1211/1221	1218/1228	1219	1218	1208/1228/1261	v _{ring} (X sens.)	13
1332	1335		1333			
1381	1383	1383	1383	1382	δ(CH ₃)	19a
1496	1504		1503	1510	v(CC, CN) _{ring}	8b
1563	1567		1569		v(CC) _{ring}	8a
1605	1615	1619	1616	1645	v(CC) _{ring}	
2869		2869	2875	2866	v _s (CH ₃)	
2923	2934	2933	2933	2933	v _s (CH ₃) _{FR}	
2982	2997		2997	3011	comb.	
3032					v(CH) _{ring}	20a,20b
3051	3068	3068	3066	3105	v(CH) _{ring}	2

^a From References 51-57.^b α = backbone deformation; v = stretch; δ = bend^c (hy) = hydrated, (dehy) = dehydrated

FTIR Spectroscopy of 4-Picoline. Bands due to silica and water dominate the FTIR spectrum of adsorbed 4-picoline. Therefore, only small spectral regions wherein picoline bands can be identified above the background are presented.

Figure S2 shows FTIR spectra of neat 4-picoline and neat 4-picoline adsorbed to silica from the vapor phase in the $\nu(\text{CC})_{\text{ring}}$ and $\nu(\text{CH})$ regions, respectively. Table S4 contains FTIR spectral bands and their assignments for these systems. As in the Raman spectrum of this system, shifts to higher frequency of up to $\sim 10 \text{ cm}^{-1}$ are observed upon adsorption. Evidence for both hydrogen-bonded and physisorbed 4-picoline species is observed in these data. Most notably, the $\nu(\text{CC})$ mode at 1606 cm^{-1} in neat 4-picoline appears as a doublet with peaks at 1607 and 1617 cm^{-1} in the spectrum of adsorbed 4-picoline. Thus, the FTIR data, although limited by serious interferences from silica and water, serve to corroborate the proposed N atom hydrogen-bonding mechanism for 4-picoline adsorption to silica.

TABLE S4. Peak Frequencies and Assignments for FTIR Spectra of Neat and Adsorbed 4-Picoline.

FTIR Spectral Bands (cm ⁻¹)			
Neat 4-Picoline	4-Picoline on SiO ₂ (hy) ^c	Assignment ^{a,b}	Wilson Notation
1381	1384	$\delta(\text{CH}_3)$	
1413	1425	$\nu(\text{CC, CN})_{\text{ring}}$	19b
1446	1450		
1497	1497	$\nu(\text{CC, CN})_{\text{ring}}$	19a
1511	1511		
1563	1568	$\nu(\text{CC})_{\text{ring}}$	8b
1606	1607/1617	$\nu(\text{CC})_{\text{ring}}$	8a
2866	2868	$\nu_s(\text{CH}_3)$	
2895	2895		
2923	2927	$\nu_s(\text{CH}_3)_{\text{FR}}$	
2964	2963	$\nu_{\text{as}}(\text{CH}_3)$	
2992	2993	comb.	
3029	3031	$\nu(\text{CH})_{\text{ring}}$	
3070	3070	$\nu(\text{CH})_{\text{ring}}$	

^a From References 51-57.

^b ν = stretch; δ = bend

^c (hy) = hydrated, (dehy) = dehydrated

TABLE S5. Peak Frequencies and Assignments for Raman Spectra of Neat and Adsorbed 2-Picoline.

Neat 2-Picoline	Raman Spectral Bands (cm ⁻¹)				Wilson Notation
	0.1 M Aqueous 2-Picoline	2-Picoline on SiO ₂ (hy) ^c	2-Picoline on SiO ₂ (dehy) ^c	1.0 M Aqueous pH < 3	
547	550	549	548	543	ring (X sens.)
629	636	638	637	629	α(CCC)
800/811	804	802	801/812	808	ring (X sens.)
998	1010	1015	1014	1016	v _{ring}
1050	1055	1053	1055	1050	δ(CH)
1102	1107	1106	1107	1112	δ(CH)
1150	1156	1154	1154	1171	δ(CH)
1236	1242	1242	1241	1249	v _{ring} (X sens.)
1296	1300	1301	1300	1299	δ(CH)
1377	1384	1385	1386	1388/1411	δ(CH ₃)
1430	1433		1435		v(CC, CN) _{ring}
1570	1574	1577	1576	1632	v(CC) _{ring}
1591	1601	1607	1605	1648	v(CC) _{ring}
2863		2870	2874	2867	v _s (CH ₃)
2924	2936	2935	2937	2939	v _s (CH ₃)/FR
3014		3024	3033	3071	v(CH) _{ring}
3048	3068	3066	3068	3097	v(CH) _{ring}
3061			3084	3113	v(CH) _{ring}
3139		3150	3153		comb.

^a From References 51-57.^b α = backbone deformation; v = stretch; δ = bend^c (hy) = hydrated, (dehy) = dehydrated

FTIR Spectroscopy of 2-Picoline. FTIR data for adsorbed 2-picoline are again limited by the strong absorption of silica and water. Figure S3 shows the FTIR spectra of neat 2-picoline and neat 2-picoline adsorbed to silica from the vapor phase. Table S6 lists the FTIR peak frequencies and assignments for these systems. As in the Raman spectra, shifts toward slightly higher frequency are observed upon adsorption. The FTIR spectra contain no evidence for physisorbed multilayers, and are consistent with 2-picoline adsorption through hydrogen bonding. Despite the limitations of FTIR for such systems, the frequency shifts corroborate the Raman data and support the proposed hydrogen bonding.

TABLE S6. Peak Frequencies and Assignments for FTIR Spectra of Neat and Adsorbed 2-Picoline.

FTIR Spectral Bands (cm ⁻¹)			
Neat 2-Picoline	2-Picoline on SiO ₂ (hy) ^c	Assignment ^{a,b}	Wilson Notation
1434	1434	v(CC, CN) _{ring}	19b
1451	1450/1457	v(CC, CN) _{ring}	
1478	1486	v(CC, CN) _{ring}	19a
1570	1576	v(CC) _{ring}	8b
1593	1605	v(CC) _{ring}	8a
2862	2854	v _s (CH ₃)	
2925	2929	v _s (CH ₃) _{FR}	
2959	2961	v _a (CH ₃)	
3012	3013/3022	v(CH) _{ring}	
3048		v(CH) _{ring}	20a
3061		v(CH) _{ring}	2
3068	3068	v(CH) _{ring}	
3085		v(CH) _{ring}	

^a From References 51-57.^b v = stretch^c (hy) = hydrated, (dehy) = dehydrated

SI FIGURE CAPTIONS

Figure S1. FTIR spectra of (a) hydrated silica; (b) dehydrated silica.

Figure S2. FTIR spectra of (a), (c) neat 4-picoline; (b), (d) 4-picoline adsorbed to hydrated silica by vapor phase exposure.

Figure S3. FTIR spectra of (a), (c) neat 2-picoline; (b), (d) 2-picoline adsorbed to hydrated silica by vapor phase exposure.





