

Supplementary Material to:

A combined Raman, DFT and MD
study of the solvation dynamics and
the adsorption process of pyridine in
silver hydrosols

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S	Assignment	pyridine (liq.)			pyridine (aqueous sol.)			pyridine (Ag colloid)					
		Raman	Calc. A	Calc. B	Calc. C	Raman	Calc. A	Calc. B	Calc. C	Raman	Calc. A	Calc. B	Calc. C
A ₂	Ag...N stretch	379 ^a	376	381	377		382	385	383	210 ^b br	208	203	205
B ₁	$\nu(13)$	407 w	410	411	409		394	395	397		391	390	388
A ₁	$\nu(27)$	604 w/m	599	594	593		613	607	608		420	419	419
B ₂	$\nu(10)$	653 m	648	642	643		646	640	640	623 w	637	631	632
B ₁	$\nu(22)$	709 vvw	729	725	727			722	724	649 w/m	641	636	637
B ₁	$\nu(26)$	750 vvw	762	761	762		769	766	766	708 w	704	706	709
A ₂	$\nu(25)$	885 w	918	915	916		921	918	912		904	907	909
B ₁	$\nu(12)$	942 vw	967	968	971		978	977	976	942 vw	977	978	979
A ₁	$\nu(24)$	992 vvs	959	962	971		978	979	992	1008 vvs	992	992	1005
A ₂	$\nu(9)$	980 sh	1008	1011	1013		1018	1020	1017		1015	1016	1017
A ₁	$\nu(11)$	1031 vs	1020	1013	1018		1022	1014	1019		1033	1027	1029
B ₁	$\nu(8)$	1020 vvw	1041	1040	1038		1046	1044	1042	1036 vvs	1061	1056	1054
B ₂	$\nu(23)$	1052 vvw	1054	1050	1059		1064	1058	1070		1077	1071	1082
A ₁	$\nu(21)$	1069 w	1068	1062	1070		1068	1062	1070	1069 m	1066	1062	1073
B ₂	$\nu(7)$	1150 w	1169	1156	1160			1159	1164	1197 sh	1189	1175	1180
B ₂	$\nu(20)$	1217 m	1224	1215	1223		1227	1218	1224	1221 m	1237	1227	1235
A ₁	$\nu(6)$	1290 ^a	1282	1273	1301		1290	1279	1312	1299 vw	1295	1285	1315
B ₂	$\nu(19)$	1356 vvw	1367	1353	1356		1369	1356	1358		1379	1368	1370
B ₂	$\nu(18)$	1438 w	1438	1431	1439		1444	1436	1446	1452 vw	1459	1450	1460
B ₂	$\nu(17)$	1483 w	1466	1459	1467		1473	1465	1473	1487 vw	1481	1474	1482
A ₁	$\nu(5)$	1573 w/m	1574	1577	1596		1575	1579	1598	1575 w/m	1571	1573	1593
B ₂	$\nu(16)$	1582 m	1576	1581	1600		1588	1593	1612	1599 m	1602	1607	1627
A ₁	$\nu(4)$												

Table 1S: Computed and measured vibrational frequencies for the pyridine molecule, the pyridine/water complex and the pyridine/Ag⁺ complex. S = symmetry species of pyridine. Calc. A = BLYP/CEP-31G; Calc. B = B3LYP/CEP-31G; Calc. C = B3PW91/CEP-31G. ^a ref: [1]; ^b Ag hydrosol without chloride anions.

S	Assignment	pyridine (liq.)			pyridine (aqueous sol.)			pyridine (Ag colloid)					
		Raman	Calc. A	Calc. B	Calc. C	Raman	Calc. A	Calc. B	Calc. C	Raman	Calc. A	Calc. B	Calc. C
A ₂	Ag-N stretch												
B ₁	$\nu(13)$	379 a	373	377	374		382	383	381	210 ^b br	208	200	202
A ₁	$\nu(27)$	407 w	418	416	414		391	393	397		391	389	387
B ₂	$\nu(10)$	604 w/m	607	598	597		613	613	614		420	423	422
B ₁	$\nu(22)$	653 m	660	650	650	615 w/m	646	648	648	623 w	637	638	639
B ₁	$\nu(26)$	709 vvw	723	715	716	649 m	726	716	716	649 w/m	641	644	644
A ₂	$\nu(25)$	750 vvw	764	757	758		769	761	762	708 w	775	764	766
B ₁	$\nu(12)$	885 w	903	894	895		921	897	896		904	885	887
A ₁	$\nu(24)$	942 vw	943	939	942		978	952	952	942 vw	977	955	957
A ₂	$\nu(9)$	992 vvs	966	961	968	1000 vvs	978	978	988	1008 vvs	992	991	1002
A ₁	$\nu(11)$	980 sh	991	989	990		1018	998	996		1015	996	995
B ₁	$\nu(8)$	1031 vs	1026	1013	1018	1032 vs	1022	1015	1021		1033	1030	1033
B ₂	$\nu(23)$	1020 vvw	1025	1019	1017		1046	1023	1020	1036 vvs	1061	1036	1033
A ₁	$\nu(21)$	1052 vvw	1060	1047	1054		1064	1056	1064		1077	1068	1076
B ₂	$\nu(7)$	1069 w	1072	1060	1066	1069 w	1068	1060	1066	1069 m	1066	1058	1067
A ₁	$\nu(20)$	1150 w	1182	1161	1165		1172	1164	1168		1189	1179	1183
B ₂	$\nu(6)$	1217 m	1231	1214	1220	1216 m	1227	1215	1220	1197 sh	1237	1222	1228
B ₂	$\nu(19)$	1290 a	1291	1271	1293		1290	1276	1300	1221 m	1295	1285	1309
B ₂	$\nu(18)$	1356 vvw	1378	1355	1357		1369	1356	1357	1299 vw	1379	1363	1364
B ₂	$\nu(17)$	1438 vvw	1445	1428	1435		1444	1432	1440		1459	1442	1451
A ₁	$\nu(5)$	1483 w	1473	1457	1463	1480 vw	1473	1462	1469	1452 vw	1481	1468	1475
B ₂	$\nu(16)$	1573 w/m	1574	1568	1584	1574 w/m	1575	1570	1587	1575 w/m	1571	1565	1582
A ₁	$\nu(4)$	1582 m	1576	1570	1586	1592 m	1588	1579	1601	1599 m	1602	1592	1609

Table 2S: Computed and measured vibrational frequencies for the pyridine molecule, the pyridine/water complex and the pyridine/Ag⁺ complex. S = symmetry species of pyridine. Calc. A = BLYP/LanL2DZ; Calc. B = B3LYP/LanL2DZ; Calc. C = B3PW91/LanL2DZ. ^a ref: [1]; ^b Ag hydrosol without chloride anions.

S	Assignment	pyridine (liq.)		pyridine (aqueous sol.)		pyridine (Ag colloid)				
		Raman	Calc. A	Calc. B	Raman	Calc. A	Calc. B	Raman	Calc. A	Calc. B
A ₂	Ag-N stretch									
B ₁	$\nu(13)$	379 a	377	373			210 bbr	204	199	
A ₁	$\nu(27)$	407 w	408	406				384	382	
B ₂	$\nu(10)$	604 w/m	605	613				419	417	
B ₁	$\nu(22)$	653 m	605	663			623 w	644	653	
B ₁	$\nu(26)$	709 vvw	707	702			649 w/m	647	661	
A ₂	$\nu(25)$	750 vvw	742	733			708 w	697	702	
B ₁	$\nu(12)$	885 w	885	843			747	747	741	
A ₁	$\nu(24)$	942 vw	904	872			882	882	847	
A ₂	$\nu(9)$	992 vvs	954	956			942 vw	904	883	
A ₁	$\nu(11)$	980 sh	920	894			1008 vvs	988	991	
A ₁	$\nu(8)$	1031 vs	1034	1039			1036 vvs	920	891	
B ₁	$\nu(23)$	1020 vvw	915	908				1065	1069	
B ₂	$\nu(21)$	1052 vvw	1056	1061				941	928	
A ₁	$\nu(7)$	1069 w	1077	1088				1080	1083	
B ₂	$\nu(20)$	1150 w	1189	1199			1069 w	1074	1082	
A ₁	$\nu(6)$	1217 m	1237	1245			1197 sh	1209	1218	
B ₂	$\nu(19)$	1290 a	1294	1285			1221 m	1255	1261	
B ₂	$\nu(18)$	1356 vvw	1380	1396			1299 vw	1324	1316	
B ₂	$\nu(17)$	1438 vvw	1451	1463				1402	1414	
A ₁	$\nu(5)$	1483 w	1479	1494			1452 vw	1476	1481	
B ₂	$\nu(16)$	1573 w/m	1580	1582			1487 vw	1500	1511	
A ₁	$\nu(4)$	1582 m	1591	1588			1575 w/m	1586	1586	
							1592 m	1627	1622	

Table 3S: Computed and measured vibrational frequencies for the pyridine molecule, the pyridine/water complex and the pyridine/Ag⁺ complex. S = symmetry species of pyridine; Calc. A = MP2/CEP-31G; Calc. B = MP2/LANL2DZ; ^a ref: [1]; ^b Ag hydrosol without chloride anions.

BLYP		B3LYP		B3PW91		MP2	
CEP-31G	LanL2DZ	CEP-31G	LanL2DZ	CEP-31G	LanL2DZ	CEP-31G	LanL2DZ
106	96	103	94	108	97	128	120
372	371	380	377	376	374	379	375
411	421	414	419	412	417	414	412
611	620	605	611	605	611	623	632
645	657	640	648	640	648	649	662
720	719	718	712	720	713	702	700
763	761	764	757	764	758	743	735
917	900	915	892	916	893	889	845
974	950	975	946	977	948	902	870
974	978	976	974	987	982	916	886
1013	993	1014	992	1017	992	921	909
1021	1028	1016	1015	1018	1020	976	977
1045	1028	1044	1022	1043	1020	1045	1047
1063	1065	1058	1053	1067	1061	1070	1071
1065	1070	1060	1058	1069	1065	1075	1086
1173	1186	1160	1164	1165	1169	1195	1205
1225	1229	1216	1212	1223	1218	1243	1248
1290	1296	1279	1275	1310	1299	1312	1298
1368	1375	1356	1354	1358	1355	1390	1402
1446	1450	1438	1432	1447	1440	1462	1469
1471	1475	1465	1459	1472	1466	1489	1499
1573	1575	1577	1569	1596	1586	1583	1584
1589	1584	1593	1578	1613	1595	1608	1602

Table 4S: Computed vibrational frequencies for the pyridine/Ag(0) complex.

References

- [1] T. D. Klots, *Spectrochim. Acta Part. A*, 1998, **54**, 1481–1498.