Supporting information

Complexes of Molecular and Ionic Character in the Same Matrix Layer: Infrared Studies of the Sulfuric Acid/Ammonia System.

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Table S1. Observed and calculated wave numbers (/cm^{-1})of H_2SO_4.

		B3LYP/aug-cc-pVTZ		B3LYP/aug-cc-pVQZ		
Mode	Obs.[a]	Calc.[b]	Scaled [c]	Calc.[b]	Scaled [d]	Interpretation
ν_1	3570	3751 (46)	3571	3792 (56)	3571	Sym O-H str
ν_2	1216	1185 (163)	1214	1242 (173)	1214	Sym S=O str
ν_3	1136	1151 (74)	1138	1154 (67)	1139	Sym SOH bend
ν_4	831	786 (107)	828	842 (111)	830	Sym S-O str
ν_5	548	521 (22)	551	546 (43)	551	O=S=O bend
ν_6	422	418 (13)	428	442 (14)	426	O-S=O twist
ν_7	379	356 (1)	377	377 (2)	377	O-S=O bend
ν_8	224	229 (103)	218	246 (104)	221	Sym OH tors
ν_9	3567	3747 (203)	3567	3788 (236)	3567	Antisym O-H str
ν_{10}	1452	1430 (287)	1459	1495 (273)	1459	Antisym S=O str
ν_{11}	1157	1163 (86)	1157	1172 (94)	1156	Antisym SOH bend
ν_{12}	882	840 (322)	886	895 (329)	885	Antisym S-O str
ν_{13}	558	531 (22)	562	556 (29)	562	O-S=O rock
ν_{14}	506	477 (40)	501	498 (43)	501	O=S=O wag
ν_{15}	288	307 (56)	283	332 (57)	281	Antisym OH tors

[a] Data from ref [5]. [b] Infrared intensity /km mol^{-1} in paranthesis. [c] Scale factors: $f_{O\text{-}H}$ = 0.906; $f_{S\text{-}O}$ = 1.114; $f_{S=O}$ = 1.044; f_{OSO} = 1.118; f_{SOH} = 0.976; f_{OSOH} = 0.852. [d] Scale factors: $f_{O\text{-}H}$ = 0.902; $f_{S\text{-}O}$ = 1.083; $f_{S=O}$ = 1.016; f_{OSO} = 1.071; f_{SOH} = 0.983; f_{OSOH} = 0.777.

Table S2. Observed and calculated (B3LYP/aug-cc-pVTZ) wave numbers of NH_3.

Mode	Obs. [a] /cm^{-1}	Calc.[b] /cm^{-1}	Scaled [c] /cm^{-1}	Interpretation
ν_1 (A_1)	3336	3469 (4)	3319	Sym N-H str
ν_2 (A_1)	950	1025 (141)	950	H-N-H umbrella
ν_3 (E)	3414	3588 (4)	3432	Antisym N-H str
ν_4 (E)	1628	1664 (16)	1628	Antisym H-N-H def

[a] Data from ref [20]. [b] Infrared intensity /km mol^{-1} in paranthesis. [c] Scale factors: $f_{N\text{-}H}$ = 0.915; $f_{s\text{-}HNH}$ = 0.858; $f_{a\text{-}HNH}$ = 0.952.

Table S3. Calculated (B3LYP/aug-cc-pVQZ) harmonic and anharmonic wave numbers of the isolated HSO_4^- ion.

Mode	Calc.[a] /cm^{-1}	Scaled [b] /cm^{-1}	Anharmonic	Interpretation
ν_1 (A´)	3803 (26)	3611	3668	OH stretch
ν_2 (A´)	1279 (352)	1288	1246	Antisym SO3 str
ν_9 (A")	1223 (397)	1234	1178	Antisym SO3 str
ν_3 (A´)	1138 (104)	1132	1091	SOH bend
ν_4 (A´)	1029 (83)	1038	1010	Sym SO3 str
ν_5 (A´)	702 (276)	728	684	S-O str
ν_{10} (A")	559 (33)	578	549	OSO def
ν_6 (A´)	548 (14)	567	540	OSO def
ν_7 (A´)	536 (12)	554	534	OSO def
ν_{11} (A")	411 (8)	418	383	OSO def
ν_8 (A´)	385 (4)	398	383	OSO def
ν_{12} (A")	90 (67)	81	147	OH tors

[a] Infrared intensity /km mol^{-1} in paranthesis. [b] Scale factors transferred from H_2SO_4.

Table S4. Calculated (B3LYP/aug-cc-pVTZ) wave numbers of isolated $H_3NHNH_3^+$.

Mode	Calc.[a] /cm^{-1}	Scaled [b] /cm^{-1}	Interpretation
ν_1	3542 (43)	3388	Antisym NH_3 str
ν_2	3542 (43)	3388	Antisym NH_3 str
ν_3	3519 (99)	3366	Antisym NH_3 str
ν_4	3519 (99)	3366	Antisym NH_3 str
ν_5	3446 (7)	3296	Sym NH_3 str
ν_6	3426 (46)	3277	Sym NH_3 str
ν_7	1750 (0)	1736	Antisym NH_3 def
ν_8	1750 (0)	1736	Antisym NH_3 def
ν_9	1728 (3024)	1715	N…H…N str
ν_{10}	1662 (10)	1622	Antisym NH_3 def
ν_{11}	1662 (10)	1622	Antisym NH_3 def
ν_{12}	1571 (105)	1545	Antisym NH_3 def
ν_{13}	1571 (105)	1545	Antisym NH_3 def
ν_{14}	1354 (81)	1259	NH_3 umbrella
ν_{15}	1262 (13)	1173	NH_3 umbrella
ν_{16}	600 (6)	600	NH_3 rock
ν_{17}	600 (6)	600	NH_3 rock
ν_{18}	390 (36)	390	N…H…N bend
ν_{19}	390 (36)	390	N…H…N bend
ν_{20}	316 (227)	316	H_3N … NH_3 str
ν_{21}	31 (0)	31	NH_3 torsion

[a] Infrared intensity /km mol^{-1} in paranthesis. [b] Scale factors transferred from NH_3 and H_2SO_4. Scale factors for intermolecular coordinates set to 1.00.

Table S5. Observed and calculated (B3LYP/aug-cc-pVTZ) wave numbers of the NH_3*H_2SO_4 complex.

Mode	Calc.[a] /cm^{-1}	Scaled [b] /cm^{-1}	Interpretation
ν_1	3765 (109)	3583	Free O-H str
ν_2	3590 (22)	3435	Antisym N-H str
ν_3	3575 (35)	3420	Antisym N-H str
ν_4	3464 (3)	3314	Sym N-H str
ν_5	2438 (2771)	2304	Bonded O-H str
ν_6	1667 (16)	1628	Antisym H-N-H def
ν_7	1660 (10)	1621	Antisym H-N-H def
ν_8	1492 (114)	1478	Bonded S-O-H bend
ν_9	1364 (221)	1385	Antisym S=O str
ν_{10}	1170 (250)	1199	Sym S=O str
ν_{11}	1157 (55)	1148	Free S-O-H bend
ν_{12}	1152 (199)	1080	NH_3 umbrella
ν_{13}	1105 (49)	1014	Bonded O-H torsion
ν_{14}	904 (266)	951	Bonded S-O str
ν_{15}	786 (162)	828	Free S-O str
ν_{16}	548 (40)	581	O=S=O bend
ν_{17}	534 (18)	563	O-S=O rock
ν_{18}	519 (26)	545	O=S=O wag
ν_{19}	442 (4)	452	NH_3 rotation
ν_{20}	406 (80)	413	Intermolecular
ν_{21}	363 (8)	383	SO_4 def
ν_{22}	340 (13)	339	NH_3 rotation
ν_{23}	261 (35)	261	Intermolecular
ν_{25}	227 (84)	216	Free O-H torsion
ν_{26}	103 (14)	103	Intermolecular
ν_{27}	90 (0)	90	NH_3 rotation
ν_{28}	41 (7)	41	Intermolecular

[a] Infrared intensity /km mol^{-1} in paranthesis. [b] Scale factors transferred from NH_3 and H_2SO_4. Scale factors for intermolecular coordinates set to 1.00.

Table S6. Observed and calculated (B3LYP/aug-cc-pVTZ) wave numbers of the NH_3*NH_3*H_2SO_4 complex.

Mode	Calc.[a] /cm^{-1}	Scaled [b] /cm^{-1}	Interpretation
ν_1	3785 (92)	3603	Free O-H str
ν_2	3583 (12)	3427	Antisym NH_2 str (Am_2)
ν_3	3573 (46)	3421	Antisym NH_2 str (Am_1)
ν_4	3532 (65)	3395	Antisym NH_3 str (Am_2)
ν_5	3501 (48)	3348	Sym NH_2 str (Am_1)
ν_6	3382 (235)	3289	Sym NH_3 str (Am_2)
ν_7	2743 (1250)	2786	N···H···N
ν_8	2124 (2464)	2232	O···H···N
ν_9	1751 (27)	1793	NH_4 def.
ν_{10}	1733 (6)	1672	NH_4 def.
ν_{11}	1686 (11)	1648	NH_3 def.
ν_{12}	1651 (3)	1614	NH_3 def.
ν_{13}	1601 (73)	1539	NH_4 def.
ν_{14}	1516 (59)	1508	NH_4 def.
ν_{15}	1396 (10)	1324	NH_4 def.
ν_{16}	1313 (388)	1303	Antisym S=O str
ν_{17}	1168 (116)	1144	NH_3 umbrella (Am_2)
ν_{18}	1142 (110)	1133	Free S-O-H bend
ν_{19}	1127 (332)	1107	Antisym S=O str
ν_{20}	991 (325)	1008	Sym S=O str
ν_{21}	762 (212)	806	Free S-O str
ν_{22}	676 (27)	684	H_3NHNH_3 def
ν_{23}	580 (67)	601	SO_4 def
ν_{24}	555 (25)	580	SO_4 def
ν_{25}	547 (10)	564	SO_4 def
ν_{26}	528 (62)	506	H_3NHNH_3 def
ν_{27}	457 (142)	454	H_3NHNH_3 def
ν_{28}	419 (15)	433	SO_4 def
ν_{29}	381 (16)	395	Intermolecular
ν_{30}	370 (11)	352	Intermolecular
ν_{31}	318 (71)	320	H_3NHNH_3 def
ν_{32}	273 (34)	265	H_3NHNH_3 def
ν_{33}	253 (97)	251	H_3NHNH_3 def
ν_{34}	193 (2)	185	NH_3 rotation (Am_2)
ν_{35}	154 (15)	154	Intermolecular
ν_{36}	139 (62)	130	Free O-H torsion
ν_{37}	93 (9)	94	Intermolecular
ν_{38}	37 (10)	35	Intermolecular
ν_{39}	26 (1)	27	Intermolecular

[a] Infrared intensity /km mol^{-1} in paranthesis. [b] Scale factors transferred from H_2O, NH_3 and H_2SO_4. Scale factors for intermolecular coordinates set to 1.00.