Supporting Information for

The donor-acceptor complexes between ammonia and sulfur trioxide. FTIR and computational study.

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Figure S2. Optimized structures referring to $(NH_3)_2SO_3$ formula. The shorter N-S bond was marked by a dashed line. Structures 1 and 6 represent true minima while the other structures are stationary states with one or two negative eigenvalues of the Hessian matrix.

Figure S3. DFT/B3LYP/aug-cc-pVTZ optimized structure of the $H_3N(SO_3)_2$ complex with the most important structural parameters.

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Table S2. DFT/B3LYP/aug-cc-pVTZ calculated harmonic wavenumbers (cm^{-1}) and intensities (km mol^{-1}) of the $H_3N{\cdot}SO_3$ (I) and $H_3N{\cdot}SO_3{\cdot}NH_3$ (II^D) complexes.

Table S3. DFT/B3LYP/aug-cc-pVTZ calculated harmonic wavenumbers (cm^{-1}) and intensities (km mol^{-1}) of the $(NH_3)_2{\cdot}SO_3$ (II^{HB}) and $NH_3(SO_3)_2$ complexes.

Table S4. Relative energies (MP2) [kcal mol^{-1}] of structures referring to $(NH_3)_2SO_3$ formula with respect to the minimum (1, II^D).

Table S5. DFT/B3LYP/aug-cc-pVTZ calculated harmonic wavenumbers (cm^{-1}) and intensities (km mol^{-1}) of the $(NH_3)_2{\cdot}SO_3$ (structure 2) – transition structure.

Figure S1. Spectra of the argon matrices obtained by entrapping thermolysis products of sulfamic acid: a, b, c, d, e – spectra recorded after 5, 10, 15, 30 and 60 min of matrix deposition, respectively. The temperature of the solid sample during deposition (ca. 165 ^{0}C).

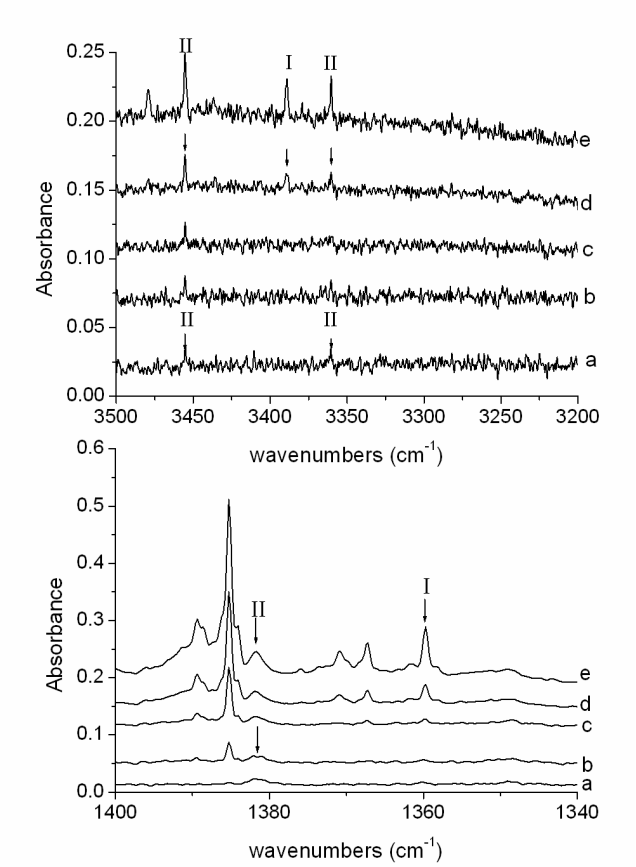

Figure S2 Optimized structures referring to $(NH_3)_2SO_3$ formula. The shorter N-S bond was marked by a dashed line. Structures 1 and 6 represent true minima while the other structures are stationary states with one or two negative eigenvalues of the Hessian matrix.

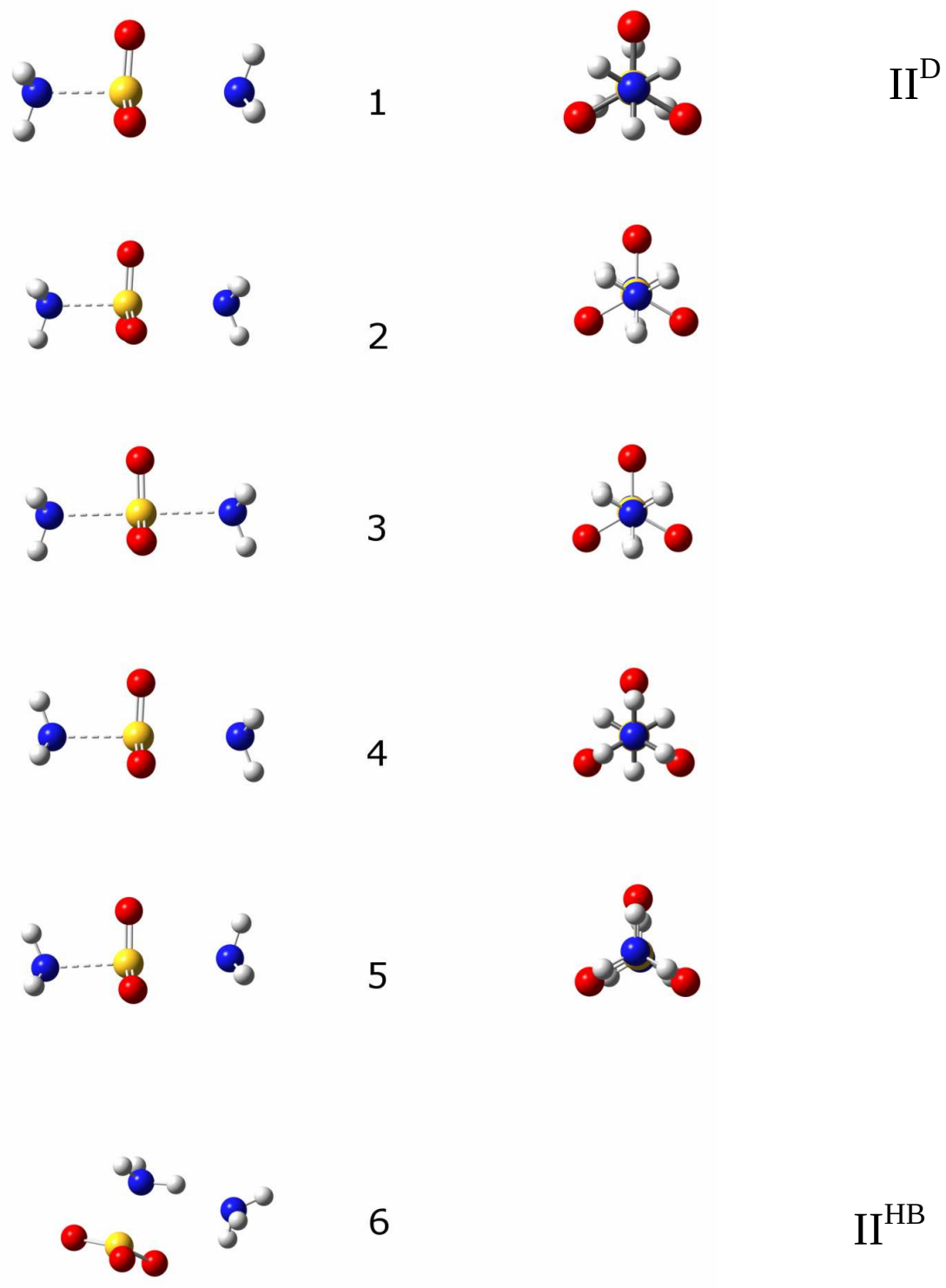

Figure S3. DFT/B3LYP/aug-cc-pVTZ optimized structure of the $H_3N(SO_3)_2$ complex with the most important structural parameters.

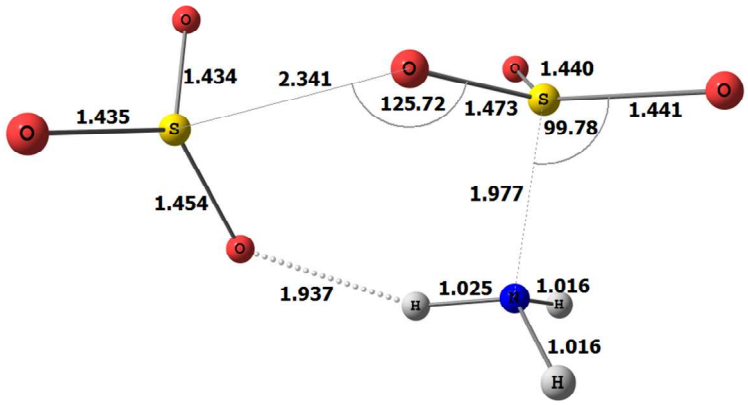

Table S1. Relative energies [kcal mol^{-1}] of structures referring to $(NH_3)_2SO_3$ formula with respect to the minimum (1, II^D). Information about the point symmetry group of the complex as well as the number of negative eigenvalues of the Hessian matrix (NegEV) are also provided. The results obtained at B3LYP level.

structure	Rel. energy	Symmetry	Minimum on PES	NegEV
1, II^D	0	C_{3v}	yes	0
2	+0.01	C_{3v}	no	1
3	+0.18	D_{3h}	no	1
4	+0.31	C_{3v}	no	1
5	+0.32	C_{3v}	no	2
6, II^{HB}	-9.92	C_1	yes	0

Table S2. DFT/B3LYP/aug-cc-pVTZ calculated harmonic wavenumbers (cm^{-1}) and intensities ($kmmol^{-1}$) of the $H_3N{\cdot}SO_3$ (I) and $H_3N{\cdot}SO_3{\cdot}NH_3$ (II^D) complexes.

NH_3-SO_3, I			**NH_3-SO_3-NH_3, II^D**		
ν [cm^{-1}]	**I**	**assign.**	**ν [cm^{-1}]**	**I**	**assign.**
3587.2	56	$\nu_{as}NH_3$	3603.1	37	$\nu_{as}NH_{3(s)}$ *
3587.0	56	$\nu_{as}NH_3$	3603.1	37	$\nu_{as}NH_{3(s)}$
3455.4	27	$\nu_{s}NH_3$	3599.5	9	$\nu_{as}NH_{3(w)}$
1636.3	29	$\delta_{as}NH_3$	3599.5	9	$\nu_{as}NH_{3(w)}$
1635.9	29	$\delta_{as}NH_3$	3474.2	1	$\nu_{s}NH_{3(w)}$
1337.0	262	$\nu_{as}SO_3$	3468.6	13	$\nu_{s}NH_{3(s)}$
1336.8	262	$\nu_{as}SO_3$	1659.4	19	$\delta_{as}NH_{3(w)}$
1203.7	160	$\delta_{s}NH_{3\ (umbrella)}$	1659.4	19	$\delta_{as}NH_{3(w)}$
1037.1	16	$\nu_{as}SO_3 + \delta_{s}NH_3$	1642.2	26	$\delta_{as}NH_{3(s)}$
722.5	15	γOSNH	1642.2	26	$\delta_{as}NH_{3(s)}$
721.7	15	γOSNH	1342.7	241	$\nu_{as}SO_3$
534.1	193	$\delta_{s}SO_3$	1342.7	241	$\nu_{as}SO_3$
498.4	14	$\delta_{s}SO_3$ + γOSNH	1132.5	161	$\delta_{s}NH_{3(s)\ (umbrella)}$
498.3	14	$\delta_{as}SO_3$+γOSNH	1031.9	52	$\delta_{s}NH_{3(w)\ (umbrella)} + \nu_{s}SO_3$
280.4	43	νNS	1021.6	119	$\nu_{s}SO_3 + \delta_{s}NH_{3(w)}$
235.5	5	τOSNH	618.7	20	$\gamma OSNH_{(s)}$
234.9	5	τOSNH	618,7	20	$\gamma OSNH_{(s)}$
100.7	0	$\delta_{as}NH_3$	487,5	9	$\gamma OSNH_{(s)}$
			487.5	9	$\gamma OSNH_{(s)}$
			475.6	284	$\delta_{s}SO_3$
			264.2	10	$\gamma OSNH_{(w)}$
			264.2	10	$\gamma OSNH_{(w)}$
			196.3	0	$\gamma OSNH_{(s,w)}$
			196.3	0	$\gamma OSNH_{(s,w)}$
			191.6	82	$\nu NS_{(s)}$
			81.0	0	γ NSN
			79.1	45	γ NSN
			71.1	23	$\tau OSNH_{(s,w)}$
			71.1	23	$\nu NS_{(w)}$
			18.9	0	$\tau OSNH_{(s,w)}$

* s, w – the wavenumber corresponds to strongly or weakly bonded ammonia molecule, respectively.

Table S3. DFT/B3LYP/aug-cc-pVTZ calculated harmonic wavenumbers (cm^{-1}) and intensities (km mol^{-1}) of the $(NH_3)_2 \cdot SO_3$ (II^{HB}) and $NH_3(SO_3)_2$ complexes.

$(NH_3)_2$-SO_3 *			**NH_3-$(SO_3)_2$** **		
ν [cm^{-1}]	**I**	**assign.**	**ν [cm^{-1}]**	**I**	**assign.**
3585.8	14	$\nu_{as}NH_{3(a)}$	3568.8	69	$\nu_{as}NH_3$
3578.8	49	$\nu_{as}NH_{3(d)}$	3506.4	143	$\nu_{as}NH_3$
3559.1	33	$\nu_{s}NH_{3(a)}$	3340.3	177	$\nu_{s}NH_3$
3497.0	66	$\nu_{s}NH_{3(d)}$	1641.1	28	$\delta_{as}NH_3$
3452.2	13	$\nu_{s}NH_{3(d)}$	1621.8	14	$\delta_{as}NH_3$
2965.8	999	νNH…N	1389.7	250	$\nu_{as}SO_{3(h)}$
1682.6	4	$\delta_{as}NH_{3(a,d)}$	1367.8	161	$\nu_{as}SO_{3(b)}$
1672.9	20	$\delta_{as}NH_{3(a)}$	1327.8	118	$\nu_{as}SO_{3(h)} + \delta_{s}NH_{3(umbrella)}$
1653.4	24	$\delta_{as}NH_{3(a)}$	1285.4	301	$\delta_{s}NH_{3\ (umbrella)}$
1617.3	5	$\delta_{as}NH_{3(d)}$	1261.2	435	$\nu_{as}SO_{3(h)}$
1339.1	236	$\delta_{s}NH_{3(d)\ (umbrella)}$	1042.1	19	$\nu_{s}SO_{3(h)}$
1318.1	191	$\delta_{s}NH_{3(d)\ (umbrella)}$	1013.9	58	$\nu_{as}SO_{3(b)}$
1305.8	245	$\nu_{as}SO_3 + \delta_{s}NH_{3(d)(umbrella)}$	867.3	22	γNH_3
1136.6	187	$\delta_{s}NH_{3(a)\ (umbrella)}$	830.6	8	γNH_3
1032.2	35	$\nu_{s}SO_3$	569.0	175	$\delta SO_{3(b)}$
929.7	27	$\gamma NH_{3(d)}$	523.0	35	$\delta SO_{3(h,b)}$
836.2	7	$\gamma NH_{3(d)}$	512.1	10	$\delta SO_{3(h)}$
566.8	194	$\delta_{s}SO_3$	508.7	3	τOSON
513.6	16	$\delta_{s}SO_3 + \gamma NH_{3(d)}$	501.4	9	τOSON
504.4	12	$\delta_{s}SO_3 + \gamma NH_{3(d)}$	462.9	222	$\delta_{s}SO_{3(h)}$
455.3	28	$\gamma NH_{3(a)}$	358.1	17	νNS
410.7	23	$\gamma NH_{3(a)}$	297.4	2	τOSON
359.5	28	νNS	277.3	11	τOSON
310.3	81	γNH…N	208.2	6	τOSON
279.9	20	τNHNH	187.2	0	τOSON
256.4	14	τNHNH	172.1	3	τOSON
202.5	18	νNH…N	159.1	34	τOSON
115.6	3	τNHNH	103.8	19	νNH…O
92.6	13	τNHNH	59.1	7	τSNHO
29.9	0	τNHNH	31.7	5	τOSON

* (a),(d) – due to ammonia molecule that is a proton acceptor or proton donor in N-H··N bond

** (b) – due to SO_3 molecule of the H_3NSO_3 adduct that forms (S)O··H-N bond·

(h) – due to SO_3 molecule that forms (S)O··H-N bond·

Table S4. Relative energies (MP2) [kcal mol^{-1}] of structures referring to $(NH_3)_2SO_3$ formula with respect to the minimum (1, II^D). Information about the point symmetry group of the complex as well as the number of negative eigenvalues of the Hessian matrix (NegEV) are also provided.

structure	Rel. energy	Symmetry	Minimum on PES	NegEV
1, II^D	0	C_{3v}	yes	0
2	+0.004	C_{3v}	*	*
3	+0.41	D_{3h}	no	1
5	+0.59	D_{3h}	no	2
6, II^{HB}	-11.46	C_1	yes	0

*the lowest vibration frequency +13 cm^{-1} indicates that the PES is almost flat with respect to the rotation of loosely bonded NH_3 around the S-N axis. The value, although positive, is within the range of numerical error expected for the frequency calculations therefore the unambiguous categorization of the stationary point is not possible.

Table S5. DFT/B3LYP/aug-cc-pVTZ calculated harmonic wavenumbers (cm^{-1}) and intensities (km mol^{-1}) of the $H_3NSO_3NH_3$ (structure 2) – transition structure.

NH_3-SO_3-NH_3, structure 2		
ν [cm^{-1}]	**I**	**assign.**
3603.6	36	$\nu_{as}NH_3$
3603.6	36	$\nu_{as}NH_3$
3599.1	9	$\nu_{as}NH_3$
3599.1	9	$\nu_{as}NH_3$
3474.0	1	$\nu_{s}NH_3$
3469.1	12	$\nu_{s}NH_3$
1657.7	19	$\delta_{as}NH_3$
1657.7	19	$\delta_{as}NH_3$
1642.6	25	$\delta_{as}NH_3$
1642.6	25	$\delta_{as}NH_3$
1342.9	240	$\nu_{as}SO_3$
1342.9	240	$\nu_{as}SO_3$
1128.6	159	$\delta_{s}NH_3$ (umbrella)
1036.4	112	$\delta_{s}NH_3$ (umbrella)
1024.2	52	$\nu_{as}SO_3 + \delta_{s}NH_3$
612.2	21	γOSNH
612.2	21	γOSNH
486.7	9	γOSNH
486.7	9	γOSNH
472.4	287	$\delta_{s}SO_3$
281.5	11	γOSNH
281.5	11	γOSNH
199.1	0	γOSNH
199.1	0	γOSNH
186.7	79	$\nu NS_{(s)}$
79.1	0	γ NSN
74.7	22	γ NSN
74.7	22	τOSNH
73.9	54	$\nu NS_{(w)}$
i13.8	0	τOSNH