# Electronic Supplementary Information

## Photochemistry of $HNSO_2$ in Cryogenic Matrices: Spectroscopic Identification of the Intermediates and Mechanism

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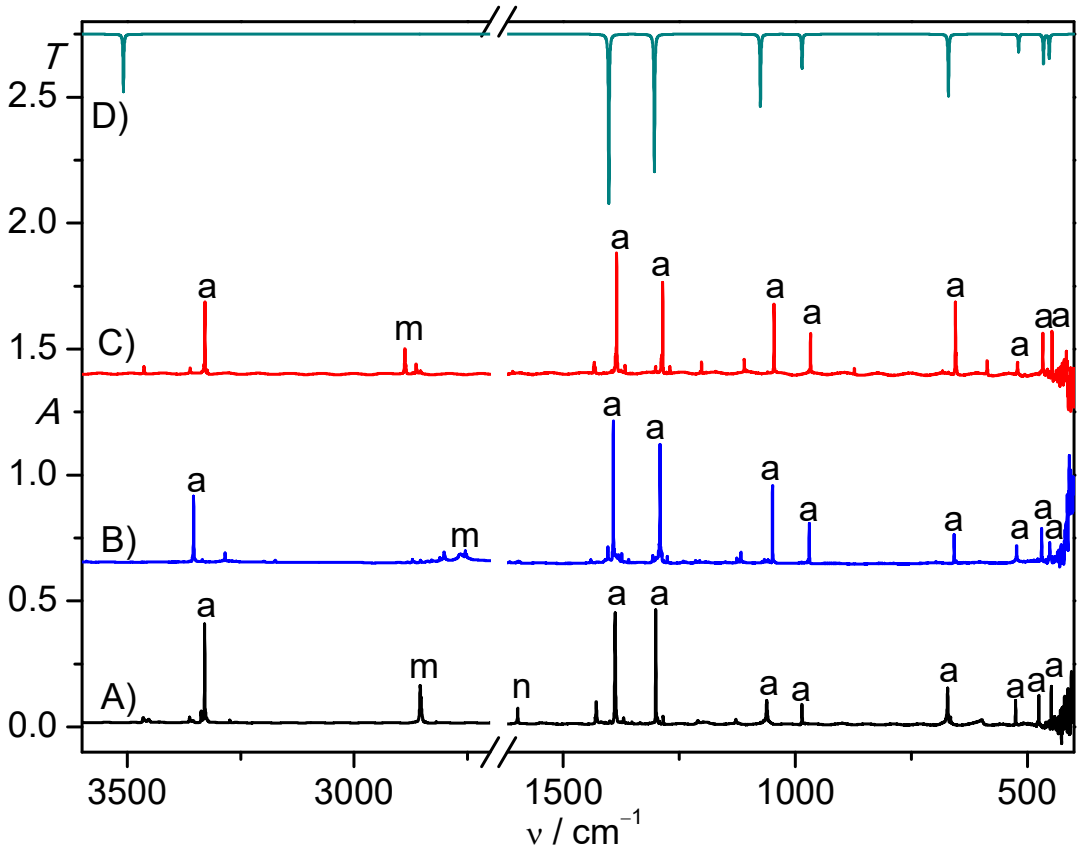


**Figure S1.** A) IR spectrum (3600–400 $cm^{-1}$) of the HVFP (high-vacuum flash pyrolysis, ca.1000 K) products of $NH_2S(O)_2Cl$ in solid $N_2$ matrix at 15.0 K; B) IR spectrum of the HVFP products of $NH_2S(O)_2Cl$ in solid Ne matrix at 2.8 K; C) IR spectrum of the HVFP products of $NH_2S(O)_2Cl$ in solid Ar matrix at 10.0 K; D) Computed IR spectrum of $HNSO_2$ (a) at B3LYP/6-311++G(3pd,3df) level. The IR bands of $HNSO_2$ (a), HCl (m), and $H_2O$ (n) are also labeled.

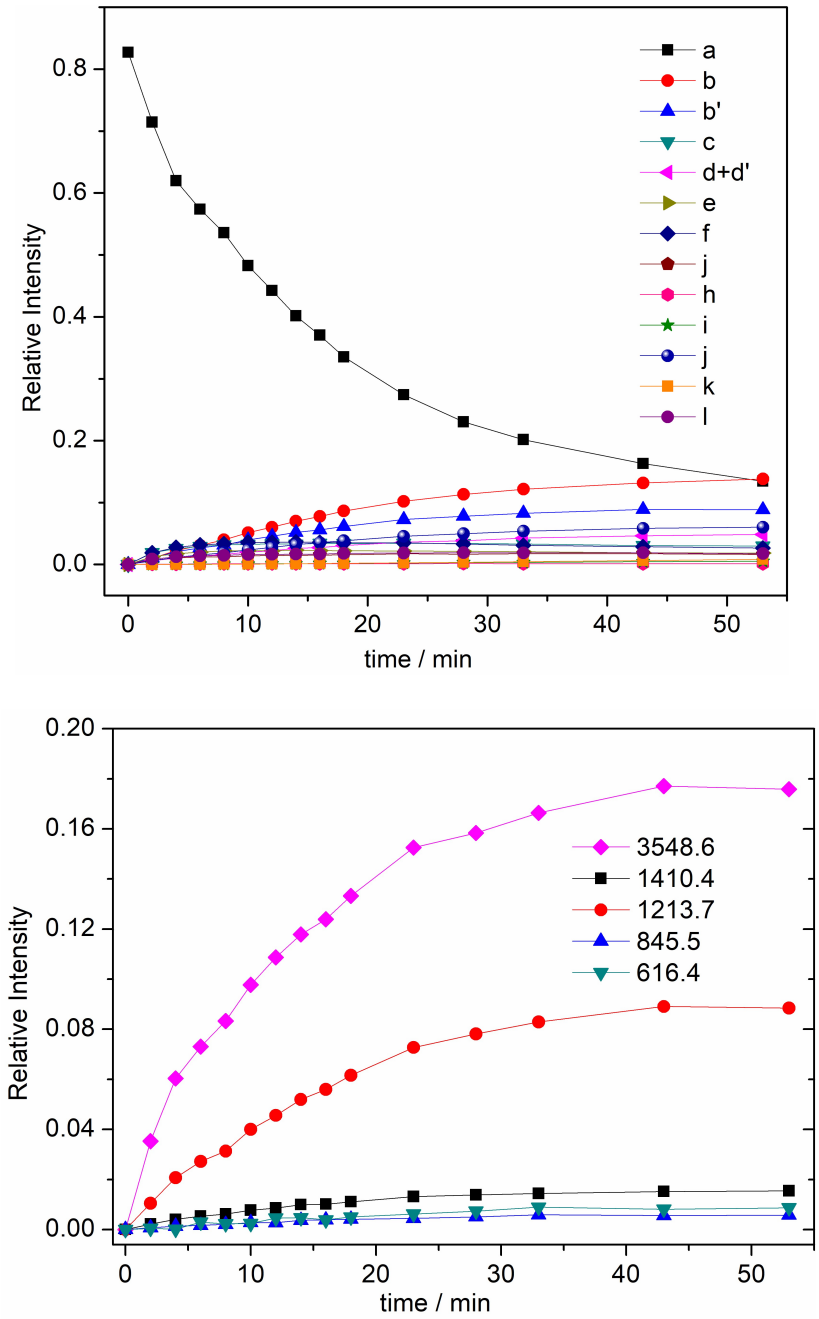


**Figure S2**. Upper: the integrated IR band intensities (unscaled) for the 193 nm laser depletion of $HNSO_2$ (a) and the concomitant formation of *syn-syn* HONSO (b, 1012.0 $cm^{-1}$), *anti-syn* HONSO (b', 1213.7 $cm^{-1}$), HOSNO (c, 1503.7 $cm^{-1}$), *syn* and *anti* HOS(O)N (d and d', 3471.3 and 3480.1 $cm^{-1}$), HS(O)NO (e, 1755.3 $cm^{-1}$), HN(O)SO (f, 1328.4 $cm^{-1}$), HOS•···•NO (g, 1839.5 $cm^{-1}$), HSONO (h, 1750.0 $cm^{-1}$), •NO (i, 1874.8 $cm^{-1}$), •OH (j, 3569.2 $cm^{-1}$), $•NO_2$ (k, 1615.9 $cm^{-1}$), and HONO (l, 1682.1 $cm^{-1}$). Lower: the integrated IR band intensities (unscaled) for *anti-syn* HONSO (b') during the 193 nm laser irradiation.

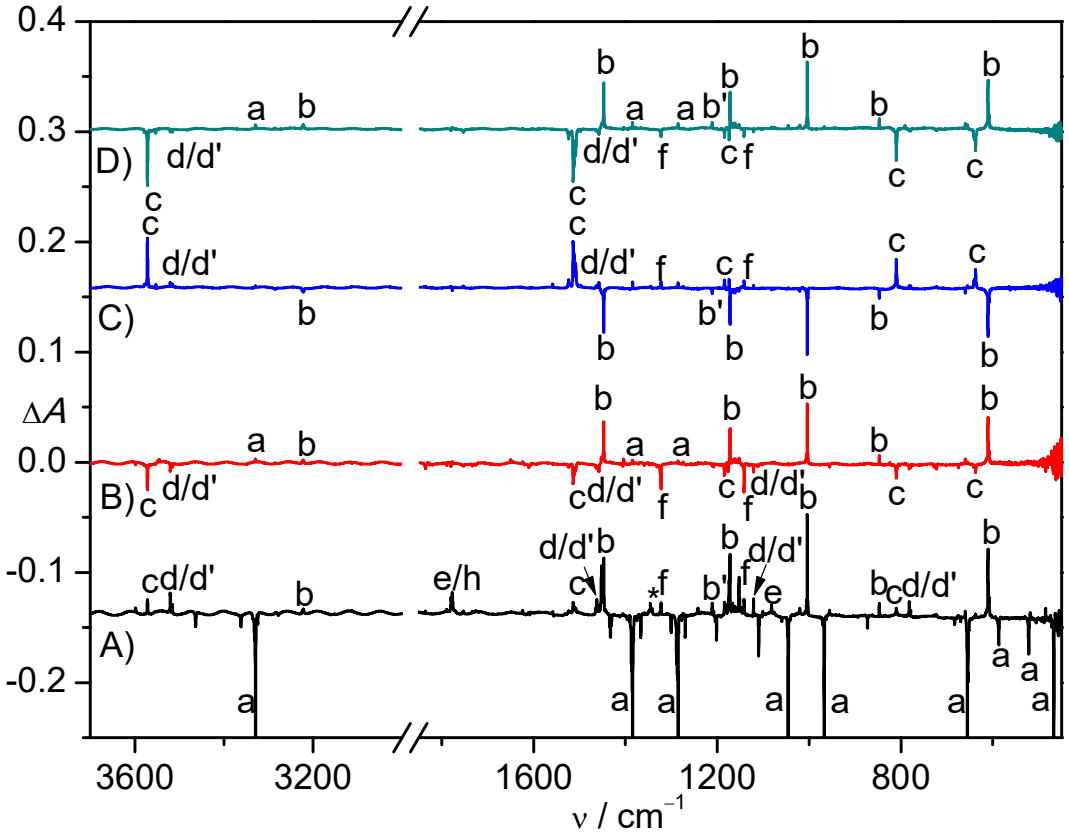


**Figure S3.** IR difference spectra (3700–450 $cm^{-1}$) showing the sequential changes of Ar matrix containing HVFP products of $NH_2S(O)_2Cl$ at 10.0 K upon 193 nm laser irradiation (60 min) (A), 365 nm irradiation (20 min) (B), 266 nm laser irradiation (20 min) (C), 365 nm irradiation (D). The IR bands of $HNSO_2$ (a), *syn-syn* HONSO (b), *anti-syn* HONSO (b'), HOSNO (c), *syn* HOS(O)N (d), *anti* HOS(O)N (d'), HS(O)NO (e), HN(O)SO (f), HSONO (h), and unknown species (*) are labelled.

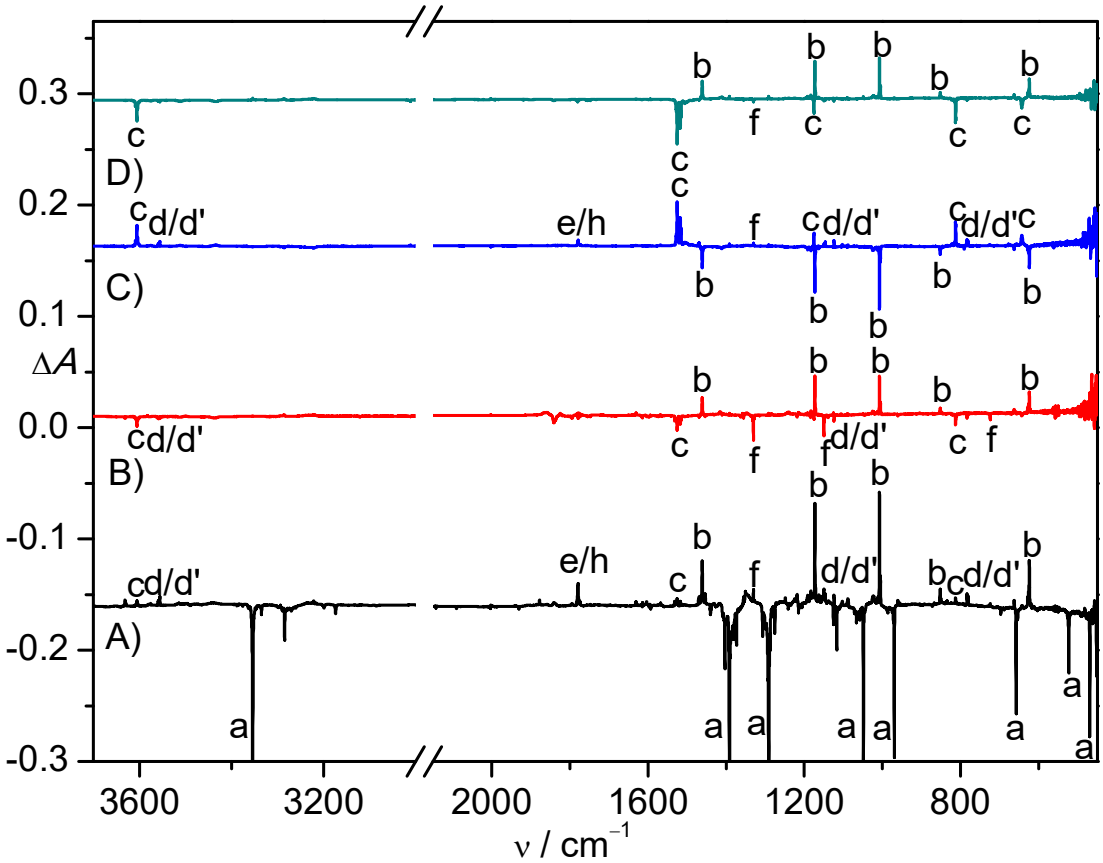


**Figure S4.** IR difference spectra (3700–450 $cm^{-1}$) showing the sequential changes of Ne matrix containing HVFP products of $NH_2S(O)_2Cl$ at 2.8 K upon 193 nm laser irradiation (35 min) (A), 365 nm irradiation (20 min) (B), 266 nm laser irradiation (20 min) (C), 365 nm irradiation (D). The IR bands of $HNSO_2$ (a), *syn-syn* HONSO (b), HOSNO (c), *syn* HOS(O)N (d), *anti* HOS(O)N (d'), HS(O)NO (e), HN(O)SO (f), and HSONO (h) are labelled.

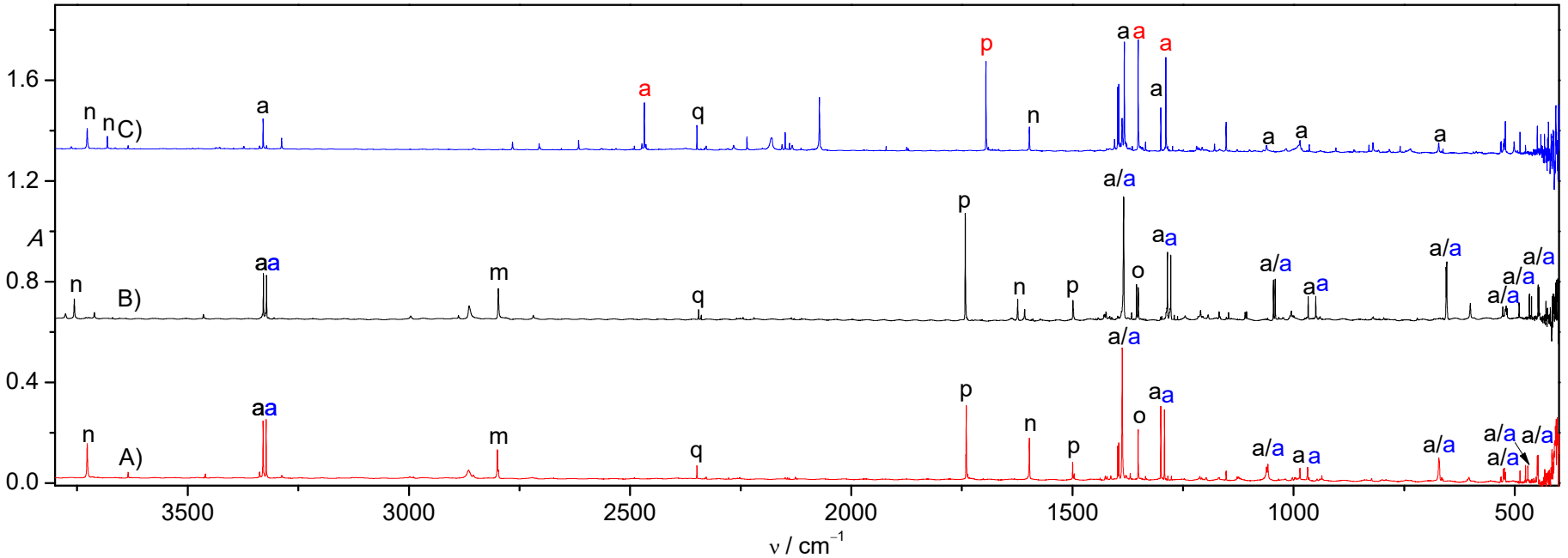


**Figure S5.** A) IR spectrum (3800–400 $cm^{-1}$) of the HVFP products of $^{15}N$-isotope labeled $CH_3OS(O)_2N_3$ in solid $N_2$ matrix at 15.0 K; B) IR spectrum of the HVFP of $^{15}N$-isotope labeled $CH_3OS(O)_2N_3$ in Ar matrix at 10.0 K; C) IR spectrum of the HVFP of $CD_3OS(O)_2N_3$ in $N_2$ matrix at 15.0 K. The IR bands of $HNSO_2$ (a), $H_2O$ (n), $SO_2$ (o), $H_2CO$ (p), and $CO_2$ (q) are labeled. The deuterated species are labelled in red color and $^{15}N$-isotope labeled species are labelled in blue color.

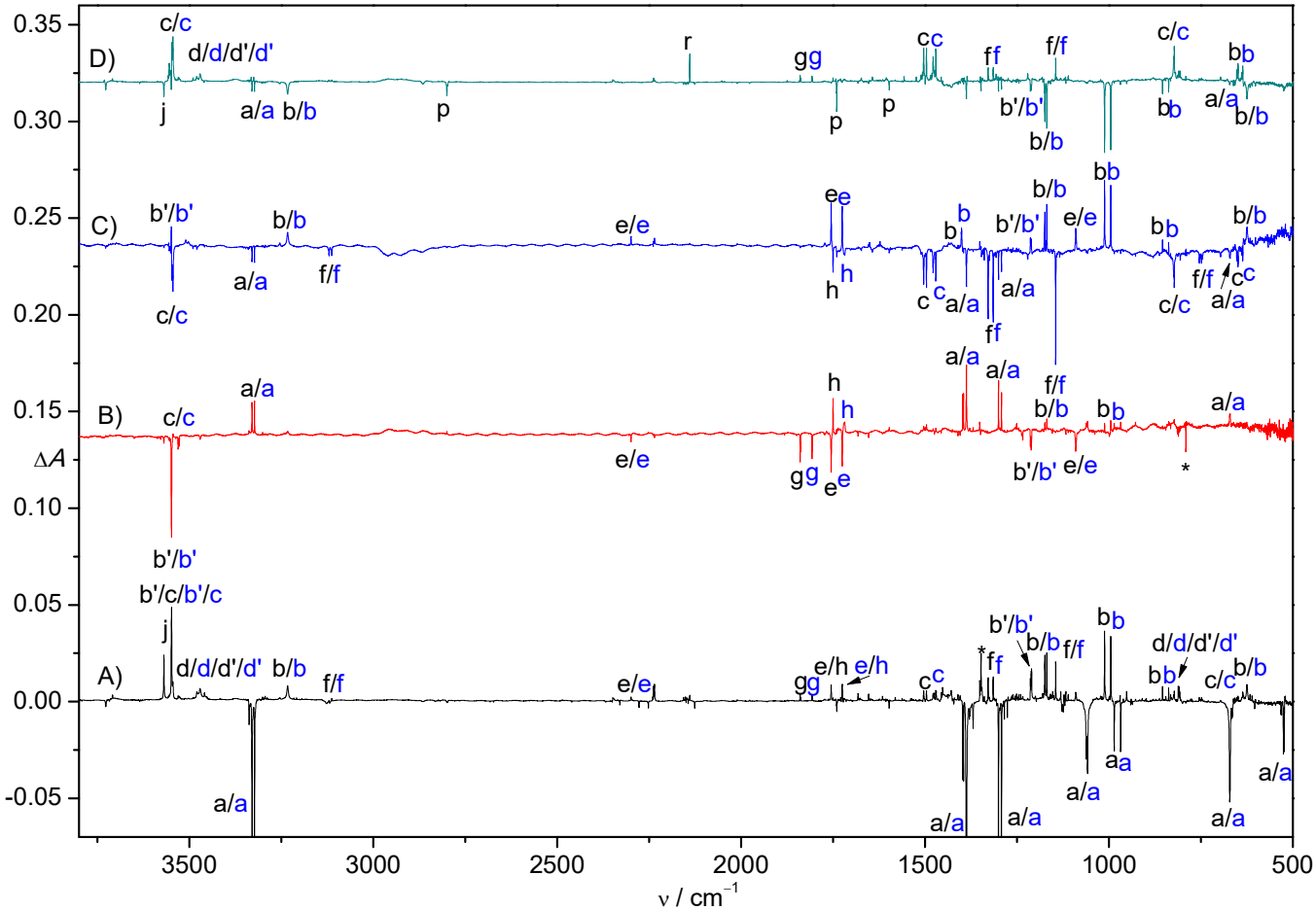


**Figure S6.** IR difference spectra (3800–500 $cm^{-1}$) showing the sequential changes of the $N_2$ matrix containing the HVFP products of $^{15}N$-isotope labeled $CH_3OS(O)_2N_3$ at 15.0 K upon 193 nm laser irradiation (35 min) (A), 830 nm irradiation (5 min) (B), 365 nm laser irradiation (20 min) (C), 266 nm irradiation (20 min) (D). The IR bands of $HNSO_2$ (a), *syn-syn* HONSO (b), *anti-syn* HONSO (b'), HOSNO (c), *syn* HOS(O)N (d), *anti* HOS(O)N (d'), HS(O)NO (e), HN(O)SO (f), HSO•···•NO radical pair (g), HSONO (h), •OH (j), $H_2CO$ (p), CO (r), and unknown species (*) are labelled. The $^{15}N$-isotope labeled species are labelled in blue color.

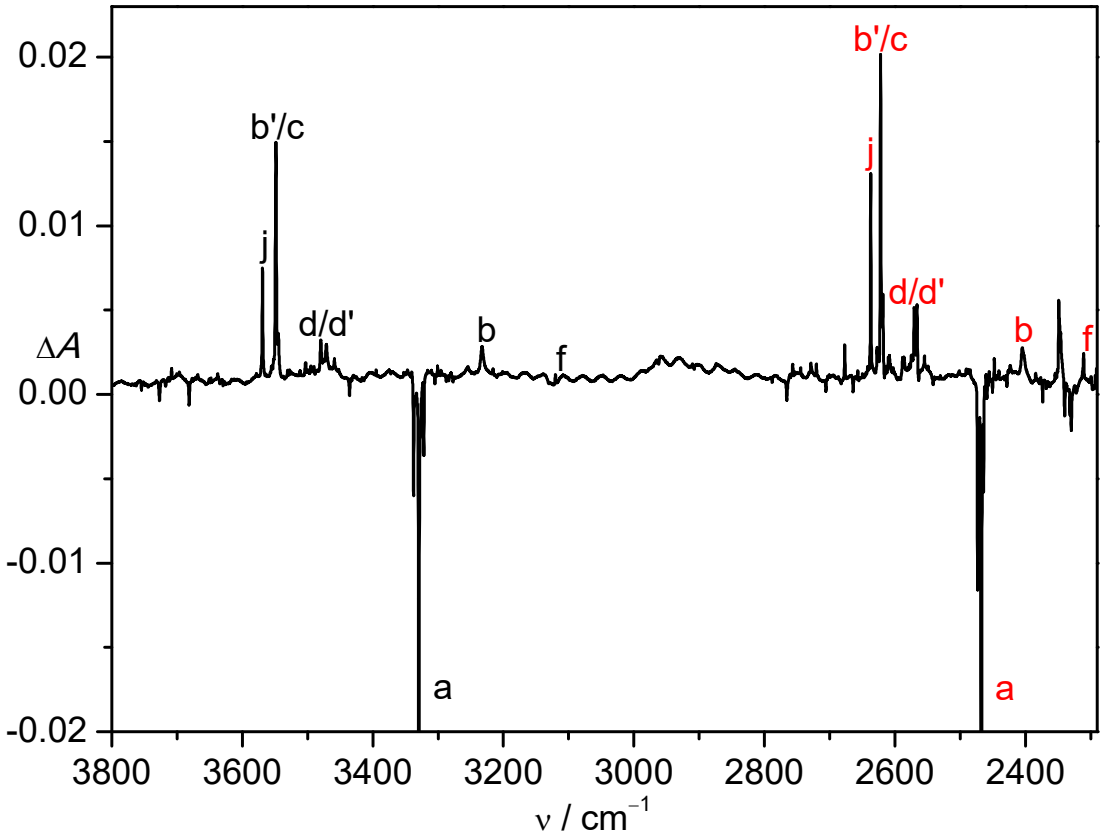


**Figure S7.** IR difference spectrum (3800–2290 $cm^{-1}$) reflecting the changes of $HNSO_2$/$DNSO_2$ in $N_2$ matrix at 15 K upon 193 nm laser irradiation (55 min). The IR bands of $HNSO_2$ (a), *syn-syn* HONSO (b), *anti-syn* HONSO (b'), HOSNO (c), *syn* HOS(O)N (d), *anti* HOS(O)N (d'), HN(O)SO (f), •OH (j) are also labelled, and deuterated species are labelled in red color.

**Table S1.** Observed and computed IR frequencies and isotopic shifts ($cm^{-1}$) for $HNSO_2$.

| $\nu_{calcd}$[a] | | $\nu_{obsd}$[b] | | | $\Delta\nu(^{14/15}N)$[c] | |
|---|---|---|---|---|---|---|
| harmonic | anharmonic | Ne | Ar | $N_2$ | calcd | obsd |
| 3508 (66) | 3350 (57) | 3354.1 | 3328.9 | 3329.6 (58) | 7.8 | 6.9 |
| 1401 (194) | 1375 (184) | 1391.7 | 1384.5 | 1387.4 (100) | 0.5 | 0.5 |
| 1303 (158) | 1278 (152) | 1291.2 | 1285.3 | 1300.5 (48) | 8.2 | 7.7 |
| 1075 (82) | 1042 (70) | 1049.0 | 1045.6 | 1061.4 (35) | 3.6 | 3.2 |
| 985 (39) | 963 (47) | 970.3 | 967.1 | 986.6 (7) | 18.1 | 17.2 |
| 670 (71) | 642 (68) | 657.9 | 655.2 | 672.6 (33) | 1.6 | 1.4 |
| 519 (20) | 515 (20) | 523.6 | 521.9 | 525.8 (7) | 2.1 | 2.1 |
| 465 (34) | 463 (31) | 469.8 | 467.0 | 475.8 (8) | 4.9 | 5.3 |
| 453 (27) | 447 (27) | 452.3 | 447.4 | 449.0 (5) | 2.1 | 1.9 |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) at the B3LYP/6-311++G(3df,3pd) level. [b]Observed IR band positions ($cm^{-1}$) in Ne, Ar, and $N_2$ matrices, the integrated relative intensities for the bands observed in $N_2$ matrix are given in parentheses. [c]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix.

**Table S2.** Observed and computed IR data for *syn-syn* HONSO.

| $\nu_{calcd}$[a] | | $\nu_{obsd}$[b] | | | $\Delta\nu(^{14/15}N)$[c] | |
|---|---|---|---|---|---|---|
| harmonic | anharmonic | Ne-matrix | Ar-matrix | $N_2$-matrix | calcd | obsd |
| 3474 (24) | 3234 (19) | 3286.9 | 3221.7 | 3232.9 (28) | 0 | <0.5 |
| 1475 (73) | 1435 (69) | 1461.5 | 1447.1 | n.o.[d] | 2.4 | 2.7 |
| 1198 (91) | 1177 (89) | 1173.0 | 1172.8 | 1174.3 (50) | 7.3 | 5.4 |
| 1053 (166) | 1020 (145) | 1007.7 | 1004.1 | 1012.0 (100) | 16.5 | 16.7 |
| 890 (19) | 864 (3) | 852.6 | 847.4 | 854.4 (10) | 17.4 | 17.0 |
| 674 (4) | 666 (4) | 666.2 | 659.8 | 661.5 (4) | 5.1 | 4.4 |
| 666 (83) | 617 (76) | 624.5 | 610.4 | 624.8 (61) | 0.5 | 0.5 |
| 460 (20) | 453 (20) | n.o. | 443.3 | n.o. | 7.7 | n.o. |
| 230 (18) | 225 (17) | n.o. | n.o. | n.o. | 0.1 | n.o. |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) at the B3LYP/6-311++G(3df,3pd) level. [b]Observed IR band positions ($cm^{-1}$) in Ne, Ar, and $N_2$ matrices, the integrated relative intensities for the bands observed in $N_2$ matrix are given in parentheses. [c]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix. [d]Not observed.

**Table S3.** Observed and computed IR data for *anti-syn* HONSO.

| $\nu_{calcd}$[a] | | $\nu_{obsd}$[b] | | $\Delta\nu(^{14/15}N)$[c] | |
|---|---|---|---|---|---|
| harmonic | anharmonic | $N_2$-matrix | Ar-matrix | calcd | obsd |
| 3781 (151) | 3602 (126) | 3548.6 (100) | n.o. | 0 | <0.5 |
| 1430 (32) | 1396 (34) | 1410.4 (6) | n.o. | 7.9 | 5.7 |
| 1240 (137) | 1220 (136) | 1213.7 (28) | 1211.0 | 2.6 | 2.2 |
| 1071 (153) | 1043 (114) | n.o.[d] | 1020.4 | 18.5 | 17.7[e] |
| 864 (42) | 843 (40) | 845.5 (6) | n.o. | 13.3 | 13.3 |
| 622 (37) | 616 (36) | 616.4 (17) | n.o. | 6.1 | 5.3 |
| 468 (117) | 477 (140) | n.o. | n.o. | 3.6 | n.o |
| 419 (15) | 426 (<1) | n.o. | n.o. | 4.4 | n.o. |
| 213 (4) | 214 (4) | n.o. | n.o. | 0.3 | n.o. |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) at the B3LYP/6-311++G(3df,3pd) level. [b]Observed IR band positions ($cm^{-1}$) in $N_2$ and Ar matrices, the integrated relative intensities for the bands observed are given in parentheses. [c]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix. [d]Not observed. [e]Observed $^{14/15}N$ isotopic shifts in Ar matrix.

**Table S4.** Observed and computed IR data for HOSNO.

| $\nu_{calcd}$[a] (*syn-syn*) | | $\nu_{calcd}$[b] (*gauche-syn*) | | $\nu_{obsd}$[c] | | | $\Delta\nu(^{14/15}N)$[d] | | |
|---|---|---|---|---|---|---|---|---|---|
| harmonic | anharmonic | harmonic | harmonic | Ne-matrix | Ar-matrix | $N_2$-matrix | *syn-syn* | *gauche-syn* | obsd |
| 3293 (50) | 2960 (39) | 3756 (89) | 3518 (57) | 3605.6 | 3571.7 | 3544.6 (74) | 0.1 | 0 | <0.5 |
| 1482 (276) | 1465 (261) | 1583 (350) | 1525 (314) | 1526.6 | 1513.9 | 1503.7 (100) | 23.1 | 27.1 | 25.6 |
| 1238 (89) | 1214 (81) | 1153 (49) | 1127 (22) | 1175.8 | 1174.3 | n.o.[e] | 0 | 0 | n.o. |
| 830 (76) | 815 (72) | 792 (104) | 775 (104) | 813.6 | 810.1 | 822.6 (39) | 0.7 | 0.3 | <0.5 |
| 725 (74) | 709 (54) | 664 (49) | 663 (47) | 643.9 | 637.3 | 649.0 (34) | 12.5 | 10.4 | 12.7 |
| 588 (61) | 512 (49) | 401 (126) | 398 (77) | n.o. | n.o. | n.o. | 1.1 | 6.2 | n.o. |
| 475 (79) | 459 (77) | 359 (4) | 355 (2) | n.o. | n.o. | n.o. | 7.4 | 2.6 | n.o. |
| 406 (15) | 393 (15) | 203 (22) | -205 | n.o. | n.o. | n.o. | 6.4 | 0.4 | n.o. |
| 264 (12) | 235 (12) | 110 (20) | -192 | n.o. | n.o. | n.o. | 1.8 | 0 | n.o. |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) for *syn-syn* HOSNO at the B3LYP/6-311++G(3df,3pd) level. [b]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) for *gauche-syn* HOSNO at the B3LYP/6-311++G(3df,3pd) level. [c]Observed IR band positions ($cm^{-1}$) in Ne, Ar and $N_2$ matrices, the integrated relative intensities for the bands observed in $N_2$ matrix are given in parentheses. [d]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix. [e]Not observed.

**Table S5**. Observed and computed IR data for *syn* HOS(O)N.

| $\nu_{calcd}$[a] | | $\nu_{obsd}$[b] | | | $\Delta\nu(^{14/15}N)$[c] | |
|---|---|---|---|---|---|---|
| harmonic | anharmonic | Ne-matrix | Ar-matrix | $N_2$-matrix | calcd | obsd |
| 3729 (132) | 3531 (113) | 3555.6 | 3515.6 | 3471.3 (100) | 0 | <0.5 |
| 1506 (78) | 1473 (68) | 1470.8 | 1464.5 | 1474.5 (47) | 20.8 | 18.4 |
| 1162 (128) | 1130 (134) | 1146.2 | 1146.8 | n.o.[d] | 6.7 | n.o |
| 1112 (39) | 1090 (27) | n.o. | n.o. | n.o. | 4.4 | n.o. |
| 771 (162) | 753 (160) | 781.2 | 778.7 | 810.2 (78) | 2.0 | 2.5 |
| 474 (34) | 468 (31) | n.o. | n.o. | n.o. | 1.8 | n.o. |
| 456 (124) | 418 (121) | n.o. | n.o. | n.o. | 0 | n.o. |
| 409 (2) | 405 (2) | n.o. | n.o. | n.o. | 6.1 | n.o. |
| 373 (3) | 367 (1) | n.o. | n.o. | n.o. | 2.7 | n.o. |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) at the B3LYP/6-311++G(3df,3pd) level. [b]Observed IR band positions ($cm^{-1}$) in Ne, Ar and $N_2$ matrices. [c]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix. [d]Not observed.

**Table S6**. Observed and computed IR data for *anti* HOS(O)N.

| $\nu_{calcd}$[a] | | $\nu_{obsd}$[b] | | | $\Delta\nu(^{14/15}N)$ [c] | |
|---|---|---|---|---|---|---|
| harmonic | anharmonic | Ne-matrix | Ar-matrix | $N_2$ | calcd | obsd |
| 3738 (134) | 3536 (120) | 3558.5 | 3520.5 | 3480.1 | 0 | <0.5 |
| 1501 (98) | 1471 (91) | 1469.1 | 1462.2 | 1469.4 | 18.9 | 17.2 |
| 1181 (37) | 1151 (30) | n.o.[d] | n.o. | n.o. | 5.8 | n.o. |
| 1137 (156) | 1115 (154) | 1124.2 | 1120.9 | 1118.2 | 6.7 | 7.4 |
| 776 (156) | 759 (143) | 783.7 | 781.8 | 811.7 | 2.0 | 2.6 |
| 498 (107) | 454 (104) | n.o. | n.o. | n.o. | 0.1 | n.o. |
| 478 (6) | 474 (6) | n.o. | n.o. | n.o. | 1.9 | n.o. |
| 411 (22) | 406 (21) | n.o. | n.o. | n.o. | 6.1 | n.o. |
| 381 (13) | 376 (13) | n.o. | n.o. | n.o. | 2.6 | n.o. |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) at the B3LYP/6-311++G(3df,3pd) level. [b]Observed IR band positions ($cm^{-1}$) in Ne, Ar and $N_2$ matrices. [c]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix. [d]Not observed.

**Table S7**. Observed and computed IR data for HS(O)NO.

| $\nu_{calcd}$[a] | | $\nu_{obsd}$[b] | | | $\Delta\nu(^{14/15}N)$[c] | |
|---|---|---|---|---|---|---|
| harmonic | anharmonic | Ne-matrix | Ar-matrix | $N_2$-matrix | calcd | obsd |
| 2357 (69) | 2189 (75) | 2295.0 | 2287.0 | 2299.5 (8) | 0 | <0.5 |
| 1839 (552) | 1809 (527) | 1780.1 | 1776.9 | 1755.3 (100) | 32.2 | 30.2 |
| 1118 (152) | 1101 (148) | 1088.0 | 1081.8 | 1088.5 (22) | 0.1 | <0.5 |
| 1038 (4) | 1024 (3) | n.o.[d] | n.o. | n.o. | 0.1 | n.o. |
| 653 (18) | 617 (14) | n.o. | n.o. | n.o. | 1.7 | n.o. |
| 596 (11) | 584 (9) | n.o. | n.o. | n.o. | 9.5 | n.o. |
| 284 (21) | 283 (21) | n.o. | n.o. | n.o. | 3.6 | n.o. |
| 230 (4) | 223 (3) | n.o. | n.o. | n.o. | 3.3 | n.o. |
| 132 (<1) | 131 (<1) | n.o. | n.o. | n.o. | 0.2 | n.o. |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) at the B3LYP/6-311++G(3df,3pd) level. [b]Observed IR band positions ($cm^{-1}$) in Ne, Ar and $N_2$ matrices, the integrated relative intensities for the bands observed in $N_2$ matrix are given in parentheses. [c]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix. [d]Not observed.

**Table S8**. Observed and computed IR data for HN(O)SO.

| $\nu_{calcd}$[a] (*syn*) | | $\nu_{calcd}$[b] (*anti*) | | $\nu_{obsd}$[c] | | | $\Delta\nu(^{14/15}N)$[d] | | |
|---|---|---|---|---|---|---|---|---|---|
| harmonic | anharmonic | harmonic | harmonic | Ne-matrix | Ar-matrix | $N_2$-matrix | *syn* | *anti* | obsd |
| 3233 (16) | 3046 (16) | 3220 (21) | 3039 (16) | 3121.1 | 3113.0 | 3120.2 (15) | 7.0 | 7.1 | 7.2 |
| 1483 (47) | 1445 (57) | 1462 (45) | 1426 (43) | n.o.[e] | n.o. | n.o. | 14.1 | 14.4 | n.o. |
| 1401 (245) | 1364 (194) | 1371 (315) | 1342 (303) | 1330.7 | 1322.3 | 1328.4 (100) | 15.6 | 15.0 | 13.8 |
| 1200 (192) | 1182 (185) | 1157 (236) | 1143 (221) | 1150.4 | 1141.6 | 1145.0 (71) | 1.1 | 0.3 | <0.5 |
| 751 (37) | 730 (35) | 836 (33) | 815 (31) | n.o. | n.o. | n.o. | 16.8 | 16.2 | n.o. |
| 736 (59) | 708 (56) | 804 (71) | 790 (68) | 724.8 | 722.5 | 754.3 (25) | 6.1 | 7.1 | 5.8 |
| 620 (7) | 610 (6) | 476 (<1) | 468 (<1) | n.o. | n.o. | n.o. | 2.9 | 3.3 | n.o. |
| 407 (2) | 398 (2) | 263 (27) | 261 (26) | n.o. | n.o. | n.o. | 5.0 | 0.9 | n.o. |
| 211 (6) | 206 (6) | 261 (26) | 258 (25) | n.o. | n.o. | n.o. | 0.2 | 2.9 | n.o. |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) for *syn*-HN(O)SO at the B3LYP/6-311++G(3df,3pd) level. [b]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) for *anti*-HN(O)SO at the B3LYP/6-311++G(3df,3pd) level. [c]Observed IR band positions ($cm^{-1}$) in Ne, Ar and $N_2$ matrices, the integrated relative intensities for the bands observed in $N_2$ matrix are given in parentheses. [d]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix. [e]Not observed.

**Table S9**. Observed and computed IR data for HOS•···•NO radical pair.

| $\nu_{calcd}$[a] | | $\nu_{obsd}$[b] | $\Delta\nu(^{14/15}N)$[c] | |
|---|---|---|---|---|
| harmonic | anharmonic | $N_2$-matrix | calcd | obsd |
| 3768 (87) | 3556 (119) | n.o.[d] | 0 | n.o. |
| 1945 (729) | 1916 (713) | 1839.5 | 35.0 | 32.4 |
| 1127 (42) | 1091 (56) | n.o. | 0 | n.o. |
| 781 (101) | 765 (7) | n.o. | 0.1 | n.o. |
| 532 (9) | 519 (7) | n.o. | 5.9 | n.o. |
| 462 (41) | 397 (37) | n.o. | 0.2 | n.o. |
| 295 (12) | 283 (14) | n.o. | 2.9 | n.o. |
| 255 (<1) | 237 (2) | n.o. | 3.4 | n.o. |
| 206 (14) | 197 (13) | n.o. | 1.4 | n.o. |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) at the B3LYP/6-311++G(3df,3pd) level. [b]Observed IR band positions ($cm^{-1}$) in $N_2$ matrix. [c]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix. [d]Not observed.

**Table S10**. Observed and computed IR data for HSONO.

| $\nu_{calcd}$[a] | | $\nu_{obsd}$[a] | | $\Delta\nu(^{14/15}N)$[c] | |
|---|---|---|---|---|---|
| harmonic | anharmonic | Ar-matrix | $N_2$-matrix | calcd | obsd |
| 2612 (6) | 2410 (7) | n.o.[d] | n.o. | 0 | n.o. |
| 1840 (309) | 1797 (268) | 1779.8 | 1750.0 | 32.4 | 30.4 |
| 1018 (6) | 978 (4) | n.o | n.o | 0.5 | n.o. |
| 814 (23) | 794 (15) | n.o. | n.o. | 6.6 | n.o. |
| 708 (15) | 699 (16) | n.o. | n.o. | 7.9 | n.o. |
| 359 (81) | 298 (109) | n.o. | n.o. | 3.7 | n.o. |
| 297 (69) | 291 (65) | n.o. | n.o. | 4.4 | n.o. |
| 248 (5) | 241 (1) | n.o. | n.o. | 0.2 | n.o. |
| 186 (11) | -67 (6) | n.o. | n.o. | 0.9 | n.o. |

[a]Computed harmonic and anharmonic IR frequencies ($cm^{-1}$) and intensities (km $mol^{-1}$) at the B3LYP/6-311++G(3df,3pd) level. [b]Observed IR band positions ($cm^{-1}$) in Ar and $N_2$ matrices. [c]Computed $^{14/15}N$ isotopic shifts ($cm^{-1}$) at the B3LYP/6-311++G(3df,3pd) level and observed $^{14/15}N$ isotopic shifts in $N_2$ matrix. [d]Not observed.

**Table S11**. Computed vertical transitions (> 190 nm) for $HNSO_2$ and its isomers at the TD-B3LYP/6-311++G(3df,3pd).

| $HNSO_2$ | | *syn-syn* HONSO | | *anti-syn* HONSO | | HOSNO | |
|---|---|---|---|---|---|---|---|
| 223 nm | *f* = 0.0013 | 286 nm | *f* = 0.0001 | 294 nm | *f* = 0.0005 | 545 nm | *f* = 0.0001 |
| 222 nm | *f* = 0.0001 | 256 nm | *f* = 0.1096 | 246 nm | *f* = 0.1204 | 296 nm | *f* = 0.0019 |
| 220 nm | *f* = 0.0036 | 224 nm | *f* = 0.0029 | 226 nm | *f* = 0.0045 | 283 nm | *f* = 0.0259 |
| | | 215 nm | *f* = 0.0036 | 222 nm | *f* = 0.0001 | 249 nm | *f* = 0.0003 |
| | | | | 193 nm | *f* = 0.0133 | 212 nm | *f* = 0.0517 |
| | | | | | | 195 nm | *f* = 0.0038 |
| | | | | | | 192 nm | *f* = 0.0153 |

| *syn* HOS(O)N | | *anti* HOS(O)N | | HS(O)NO | | HN(O)SO | |
|---|---|---|---|---|---|---|---|
| 281 nm | *f* = 0.0084 | 279 nm | *f* = 0.0134 | 849 nm | *f* = 0.0002 | 388 nm | *f* = 0.0004 |
| 244 nm | *f* = 0.0030 | 243 nm | *f* = 0.0035 | 372 nm | *f* = 0.0001 | 334 nm | *f* = 0.1401 |
| 200 nm | *f* = 0.0175 | 199 nm | *f* = 0.0116 | 275 nm | *f* = 0.0318 | 254 nm | *f* = 0.0005 |
| | | | | 255 nm | *f* = 0.0009 | 226 nm | *f* = 0.0012 |
| | | | | 248 nm | *f* = 0.0613 | 199 nm | *f* = 0.0001 |
| | | | | 215 nm | *f* = 0.2891 | 193 nm | *f* = 0.0039 |
| | | | | 204 nm | *f* = 0.0288 | | |

| HOS•···•NO | | HSONO | |
|---|---|---|---|
| 728 nm | *f* = 0.0001 | 463 nm | *f* = 0.0011 |
| 603 nm | *f* = 0.0002 | 299 nm | *f* = 0.0037 |
| 296 nm | *f* = 0.0019 | 269 nm | *f* = 0.0027 |
| 282 nm | *f* = 0.0272 | 245 nm | *f* = 0.0115 |
| 273 nm | *f* = 0.3850 | 215 nm | *f* = 0.0242 |
| 227 nm | *f* = 0.0003 | 196 nm | *f* = 0.0020 |
| 226 nm | *f* = 0.0374 | | |
| 218 nm | *f* = 0.0606 | | |
| 192 nm | *f* = 0.0384 | | |

**Table S12**. Observed H/D isotopic shifts of O–H and N–H stretching vibrations for HO•, $HNSO_2$ and its isomers.

| | $\nu$(OH)[a] | $\nu$(OD)[b] | $\Delta\nu_{calcd}$[c] | $\Delta\nu_{obsd}$[d] |
|---|---|---|---|---|
| *syn-syn* HONSO | 3232.9 | 2404.9 | 946.0 | 828.0 |
| *anti-syn* HONSO | 3548.6 | 2621.9 | 1026.7 | 926.7 |
| HOSNO | 3544.6 | 2618.4 | 1021.4 | 926.2 |
| *syn* HOS(O)N | 3471.3 | 2566.2 | 1015.0 | 905.1 |
| *anti* HOS(O)N | 3480.1 | 2570.4 | 1017.6 | 909.7 |
| •OH | 3569.1 | 2637.0 | 1012.0 | 932.1 |

| | $\nu$(NH)[e] | $\nu$(ND)[f] | $\Delta\nu_{calcd}$[c] | $\Delta\nu_{obsd}$[d] |
|---|---|---|---|---|
| $HNSO_2$ | 3329.6 | 2467.7 | 942.8 | 861.9 |
| HN(O)SO | 3120.2 | 2310.8 | 863.8 | 809.4 |

[a]Observed O–H stretching vibration in $N_2$ matrix; [b]Observed O–D stretching vibration in $N_2$ matrix; [c]Computed D isotopic shift at B3LYP/6-311++G(3df,3pd); [d]Observed D isotopic shift in $N_2$ matrix; [e]Observed N–H stretching vibration in $N_2$ matrix; [d]Observed N–D stretching vibration in $N_2$ matrix.

## Computed Atomic Coordinates (in Angstroms) and Energies (in Hartrees) for All Optimized Structures at the B3LYP/6-311++G(3df, 3pd) Level of Theory

**$HNSO_2$ (a)**

| | | | |
|---|---|---|---|
| N | -0.50843100 | -1.38968700 | 0.00000000 |
| H | 0.27352800 | -2.04321600 | 0.00000000 |
| S | 0.00000000 | 0.02783200 | 0.00000000 |
| O | -0.98511800 | 1.05955000 | 0.00000000 |
| O | 1.39580400 | 0.35616400 | 0.00000000 |

Zero-point correction= 0.023653 (Hartree/Particle)
Thermal correction to Energy= 0.027417
Thermal correction to Enthalpy= 0.028362
Thermal correction to Gibbs Free Energy= -0.002860
Sum of electronic and zero-point Energies= -604.016904
Sum of electronic and thermal Energies= -604.013140
Sum of electronic and thermal Enthalpies= -604.012195
Sum of electronic and thermal Free Energies= -604.043417

***syn-syn* HONSO (b)**

| | | | |
|---|---|---|---|
| O | -0.53221800 | -1.57060300 | 0.00000000 |
| H | 0.44790800 | -1.49388400 | 0.00000000 |
| N | -1.04351800 | -0.32077700 | 0.00000000 |
| S | 0.00000000 | 0.84492600 | 0.00000000 |
| O | 1.38930800 | 0.34816600 | 0.00000000 |

Zero-point correction= 0.023068 (Hartree/Particle)
Thermal correction to Energy= 0.027028
Thermal correction to Enthalpy= 0.027972
Thermal correction to Gibbs Free Energy= -0.003790
Sum of electronic and zero-point Energies= -603.995646
Sum of electronic and thermal Energies= -603.991687
Sum of electronic and thermal Enthalpies= -603.990743
Sum of electronic and thermal Free Energies= -604.022505

***anti-syn* HONSO (b')**

| | | | |
|---|---|---|---|
| O | -0.43339400 | -1.63509300 | 0.00000000 |
| H | -1.20703500 | -2.21237500 | 0.00000000 |
| N | -0.97424000 | -0.37612600 | 0.00000000 |
| S | 0.00000000 | 0.83045200 | 0.00000000 |
| O | 1.43673300 | 0.57984600 | 0.00000000 |

Zero-point correction= 0.023035 (Hartree/Particle)
Thermal correction to Energy= 0.027206
Thermal correction to Enthalpy= 0.028150
Thermal correction to Gibbs Free Energy= -0.004009
Sum of electronic and zero-point Energies= -603.993042
Sum of electronic and thermal Energies= -603.988871
Sum of electronic and thermal Enthalpies= -603.987926
Sum of electronic and thermal Free Energies= -604.020086

***gauche-syn* HOSNO (c)**

| | | | |
|---|---|---|---|
| O | 1.23086100 | 0.88581100 | -0.10915300 |
| H | 1.08548400 | 1.37877500 | 0.71006700 |

| | | | |
|---|---|---|---|
| O | -1.60264800 | 0.61442400 | -0.01019900 |
| S | 0.61006700 | -0.62653900 | 0.01616100 |
| N | -1.12460900 | -0.47943200 | -0.00197500 |

Zero-point correction= 0.020559 (Hartree/Particle)
Thermal correction to Energy= 0.025553
Thermal correction to Enthalpy= 0.026498
Thermal correction to Gibbs Free Energy= -0.007553
Sum of electronic and zero-point Energies= -603.985184
Sum of electronic and thermal Energies= -603.980190
Sum of electronic and thermal Enthalpies= -603.979246
Sum of electronic and thermal Free Energies= -604.013297

***syn-syn* HOSNO (c')**

| | | | |
|---|---|---|---|
| O | 1.40795100 | 0.11287200 | 0.00000000 |
| H | 1.13981100 | -0.84432000 | 0.00000000 |
| O | -0.58000700 | -1.48543000 | 0.00000000 |
| S | 0.00000000 | 0.90942400 | 0.00000000 |
| N | -1.10905100 | -0.38943000 | 0.00000000 |

Zero-point correction= 0.021198 (Hartree/Particle)
Thermal correction to Energy= 0.025399
Thermal correction to Enthalpy= 0.026343
Thermal correction to Gibbs Free Energy= -0.005792
Sum of electronic and zero-point Energies= -603.988349
Sum of electronic and thermal Energies= -603.984147
Sum of electronic and thermal Enthalpies= -603.983203
Sum of electronic and thermal Free Energies= -604.015338

***syn* HOS(O)N (d)**

| | | | |
|---|---|---|---|
| S | 0.00000000 | 0.19958700 | 0.00000000 |
| O | 1.43129600 | -0.00806300 | 0.00000000 |
| N | -0.92634100 | 1.29619400 | 0.00000000 |
| O | -0.63230900 | -1.28407600 | 0.00000000 |
| H | 0.09249400 | -1.92965000 | 0.00000000 |

Zero-point correction= 0.022774 (Hartree/Particle)
Thermal correction to Energy= 0.026880
Thermal correction to Enthalpy= 0.027824
Thermal correction to Gibbs Free Energy= -0.003998
Sum of electronic and zero-point Energies= -603.972068
Sum of electronic and thermal Energies= -603.967962
Sum of electronic and thermal Enthalpies= -603.967018
Sum of electronic and thermal Free Energies= -603.998840

***anti* HOS(O)N (d')**

| | | | |
|---|---|---|---|
| S | 0.00000000 | 0.19004000 | 0.00000000 |
| O | 1.43551400 | 0.22954300 | 0.00000000 |
| N | -1.10691500 | 1.11032800 | 0.00000000 |
| O | -0.30786700 | -1.39401500 | 0.00000000 |
| H | -1.27276700 | -1.49716900 | 0.00000000 |

Zero-point correction= 0.023024 (Hartree/Particle)
Thermal correction to Energy= 0.027078

Thermal correction to Enthalpy= 0.028022
Thermal correction to Gibbs Free Energy= -0.003713
Sum of electronic and zero-point Energies= -603.973407
Sum of electronic and thermal Energies= -603.969353
Sum of electronic and thermal Enthalpies= -603.968409
Sum of electronic and thermal Free Energies= -604.000144

**HS(O)NO (e)**

| | | | |
|---|---|---|---|
| S | 0.84037700 | -0.44372800 | -0.09860400 |
| O | 0.98070000 | 1.02487800 | 0.05235800 |
| H | 0.77628600 | -0.99022200 | 1.16939100 |
| N | -1.27855100 | -0.58719500 | -0.00482600 |
| O | -1.63975800 | 0.50015100 | 0.00289800 |

Zero-point correction= 0.018801 (Hartree/Particle)
Thermal correction to Energy= 0.023612
Thermal correction to Enthalpy= 0.024556
Thermal correction to Gibbs Free Energy= -0.009132
Sum of electronic and zero-point Energies= -603.958525
Sum of electronic and thermal Energies= -603.953715
Sum of electronic and thermal Enthalpies= -603.952771
Sum of electronic and thermal Free Energies= -603.986458

***anti* HN(O)SO (f)**

| | | | |
|---|---|---|---|
| O | -1.31985800 | -1.51077300 | 0.00000000 |
| S | 0.00000000 | 0.73678700 | 0.00000000 |
| O | 1.44833800 | 1.00255600 | 0.00000000 |
| N | -0.23918700 | -0.89803900 | 0.00000000 |
| H | 0.64646100 | -1.43658500 | 0.00000000 |

Zero-point correction= 0.022450 (Hartree/Particle)
Thermal correction to Energy= 0.026643
Thermal correction to Enthalpy= 0.027587
Thermal correction to Gibbs Free Energy= -0.004515
Sum of electronic and zero-point Energies= -603.975098
Sum of electronic and thermal Energies= -603.970905
Sum of electronic and thermal Enthalpies= -603.969961
Sum of electronic and thermal Free Energies= -604.002063

***syn* HN(O)SO (f')**

| | | | |
|---|---|---|---|
| O | -0.45928100 | -1.73977300 | 0.00000000 |
| S | 0.00000000 | 0.84157700 | 0.00000000 |
| O | 1.44087900 | 0.60119700 | 0.00000000 |
| N | -0.85432900 | -0.56789100 | 0.00000000 |
| H | -1.87248300 | -0.38138000 | 0.00000000 |

Zero-point correction= 0.022889 (Hartree/Particle)
Thermal correction to Energy= 0.026938
Thermal correction to Enthalpy= 0.027882
Thermal correction to Gibbs Free Energy= -0.004127
Sum of electronic and zero-point Energies= -603.978642
Sum of electronic and thermal Energies= -603.974593
Sum of electronic and thermal Enthalpies= -603.973649
Sum of electronic and thermal Free Energies= -604.005658

**HOS•···•NO (g)**

| | | | |
|---|---|---|---|
| H | -0.63935800 | 1.51893100 | 0.74820300 |
| N | 1.70748800 | 0.39360400 | 0.00400200 |
| O | 1.30199700 | -0.65427000 | 0.00287600 |
| O | -0.59451700 | 1.09905900 | -0.11989300 |
| S | -1.06080600 | -0.48953000 | 0.00999500 |

| | |
|---|---|
| Zero-point correction= | 0.021358 (Hartree/Particle) |
| Thermal correction to Energy= | 0.026208 |
| Thermal correction to Enthalpy= | 0.027152 |
| Thermal correction to Gibbs Free Energy= | -0.006455 |
| Sum of electronic and zero-point Energies= | -603.938430 |
| Sum of electronic and thermal Energies= | -603.933580 |
| Sum of electronic and thermal Enthalpies= | -603.932636 |
| Sum of electronic and thermal Free Energies= | -603.966243 |

**HSONO (h)**

| | | | |
|---|---|---|---|
| S | 1.24988300 | -0.22269400 | -0.08992000 |
| O | 0.06340500 | 0.91962300 | 0.06020900 |
| H | 1.23914900 | -0.70177000 | 1.17297700 |
| O | -1.49064500 | -0.73835900 | -0.01607200 |
| N | -1.40276500 | 0.40210900 | -0.01247900 |

| | |
|---|---|
| Zero-point correction= | 0.018423 (Hartree/Particle) |
| Thermal correction to Energy= | 0.023319 |
| Thermal correction to Enthalpy= | 0.024263 |
| Thermal correction to Gibbs Free Energy= | -0.009336 |
| Sum of electronic and zero-point Energies= | -603.963080 |
| Sum of electronic and thermal Energies= | -603.958183 |
| Sum of electronic and thermal Enthalpies= | -603.957239 |
| Sum of electronic and thermal Free Energies= | -603.990838 |