Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Table 1S. The optimized geometrical parameters of the monomers and different structures of the N_2O-SCS and N_2O-OCS at MP2/aug-cc-pVTZ and available experimental results. aug-cc-pVDZ values are given in the parenthesis.[a]

Species	Parameters	MP2	Species	Parameters	MP2
N_2O	$r(N_A\text{-}N_B)$	1.155 (1.173) 1.128[b]	OCS	C-S	1.566 (1.583) 1.560[b]
				$C\text{-}O_B$	1.169 (1.179) 1.160[b]
	$r(N_A\text{-}O_A)$	1.181 (1.191) 1.184[b]			
SCS	$r(C\text{-}S_A)$ = $r(C\text{-}S_B)$	1.562 (1.579) 1.554[b]	2a	$r(N_A\text{-}N_B)$	1.155(1.173)
				$r(N_A\text{-}O_A)$	1.182(1.191)
				$r(C\text{-}O_B)$	1.170(1.181)
				r(C-S)	1.564(1.581)
				$r(N_A\text{-}O_B)$	3.022(3.078)
				$r(O_A\text{-}O_B)$	3.088(3.133)
				$\theta(O_AN_AS)$	46.7(47.3)
				$\theta(O_AN_AC)$	63.2(63.3)
				$\theta(O_AN_BO_B)$	62.3(61.9)
				$\phi(O_AN_ACO_B)$	179.9(179.8)
				R_{cm}	3.792(3.900) 3.867[c]
				θ1	57.5(57.7) 63.2[c]
				θ2	129.3(130.7) 133.2[c]
				φ	-0.1(-0.2)
1a	$r(N_A\text{-}N_B)$	1.156(1.174)	2b	$r(N_A\text{-}N_B)$	1.156(1.174)
	$r(N_A\text{-}O_A)$	1.181(1.190)		$r(N_A\text{-}O_A)$	1.180(1.189)
	$r(C\text{-}S_A)$	1.564(1.581)		$r(C\text{-}O_B)$	1.171(1.181)
	$r(C\text{-}S_B)$	1.561(1.578)		r(C-S) $r(N_A\text{-}C)$	1.564(1.581) 3.496(3.588)
	$r(N_A\text{-}S_A)$	3.415(3.499)		$r(N_A\text{-}O_B)$	3.021(3.080)
	$r(O_A\text{-}C)$	3.265(3.346)		$\theta(O_AN_AO_B)$	93.9(94.5)
	$\theta(O_AN_AS_B)$	44.0(44.5)		$\theta(O_AN_AC)$	112.9(113.0)
	$\theta(O_AN_AC)$	63.6(63.9)		$\theta(O_AN_BS)$	116.6(116.3)
	$\theta(O_AN_BS_A)$	70.6(70.7)		$\phi(O_AN_ACS)$	179.8(179.9)
	$\phi(O_AN_ACS_A)$	180.0(-179.6)		R_{cm}	3.835(3.938)
	R_{cm}	3.588(3.670)		θ1	120.3(120.2)
	θ1	64.4(64.7)		θ2	49.7(48.5)
	θ2	108.9(108.7)		φ	179.7(179.9)
	φ	0.0(0.4)			
			2c	$r(N_A\text{-}N_B)$	1.156(1.174)
				$r(N_A\text{-}O_A)$	1.181(1.191)
				$r(C\text{-}O_B)$	1.168(1.179)
				r(C-S)	1.568(1.585)
				$r(O_A\text{-}O_B)$	3.347(3.415)
				$r(O_A\text{-}C)$	3.151(3.224)
				$\theta(O_AN_AO_B)$	44.4(44.5)
				$\theta(O_AN_AC)$	60.2(60.2)
				$\theta(O_AN_BS)$	67.9(67.8)
				$\phi(O_AN_ACS)$	179.9(-180.0)
				R_{cm}	3.418(3.498) 3.517[d]
				θ1	69.5(69.5) 68.5[d]
				θ2 φ	98.9(98.6) 99.6[d] 179.9(-180.0)

[a]Bond lengths are in angstrom (Å) and angles are in degrees. [b]Experimental data are taken from ref 56. [c]Experimental data are taken from ref 23. [d]Experimental data are taken from ref 24.

Table 2S. The Equilibrium rotational constants (MHz) and Dipole moment (in Debye) of the complexes of N_2O-SCS and N_2O-OCS and monomers at MP2/aug-cc-pVXZ (X=D,T).

		Rotational constants(MHz)			Dipole moment (D)
Species	Basis set	A	B	C	M
N_2O	aug-cc-pVDZ	-	12091	-	0.161
	aug-cc-pVTZ		12377 (12562)[a]		0.165 (0.167)[b]
SCS	aug-cc-pVDZ		3168		-
	aug-cc-pVTZ		3237 (3271)[a]		
OCS	aug-cc-pVDZ		5906		0.644
	aug-cc-pVTZ		6025 (6082)[a]		0.709 (0.712)[c]
1a	aug-cc-pVDZ	3227	1276	915	0.017
	aug-cc-pVTZ	3261	1264	911	0.017
2a	aug-cc-pVDZ	7354	1137	985	0.660
	aug-cc-pVTZ	7360	1201	1033	0.726
2b	aug-cc-pVDZ	7287	1119	970	0.665
	aug-cc-pVTZ	7323	1179	1016	0.731
2c	aug-cc-pVDZ	4322	1573	1153	0.632
	aug-cc-pVTZ	4426	1647	1201	0.695

[a]Experimental data from the ref 56.[b]Experimental data from the ref 56.[c]Experimental data from the ref 27.