Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

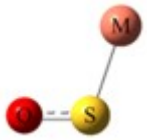
Spectroscopic Observation of Photo-Induced Metastable Linkage Isomers of Coinage Metal (Cu, Ag, Au) Sulfur Dioxide Complexes

Xing Liu, Xuefeng Wang,* Bing Xu, Lester Andrews*

1. The B3LYP calculations of selected structures with the same basis set as described in the paper. The metastable structures are marked with asterisk. For each structure, the major infrared active modes are listed in the table, and the frequencies and intensities (in parentheses) are in cm^{-1} and km mol^{-1}.

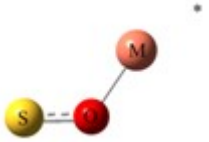
1.1 Triatomic molecules

Table 1S: Calculated frequencies for the M(η^1-SO) ($^2A''$) molecules (M = Cu, Ag, Au)



16-O	18-O	16-O/34-S	Mode assignment
	Cu(η^1-SO)		
1037.4(158)	997.8(146)	1027.4(155)	S=O str
	Ag(η^1-SO)		
1048.4(201)	1008.4(185)	1038.2(197)	S=O str
	Au(η^1-SO)		
1032.6(226)	993.2(208)	1022.6(222)	S=O str

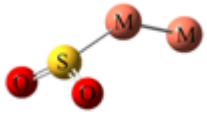
Table 2S: Calculated frequencies for the M(η^1-OS) ($^2A''$) (M = Cu,Ag, Au)



16-O	18-O	16-O/34-S	Mode assignment
	Cu(η^1-OS)		
864.8(426)	832.5(390)	856.1(420)	S=O str
	Ag(η^1-OS)		
937.9(634)	903.6(580)	928.0 (625)	S=O str
	Au(η^1-OS)		
933.2(757)	899.1(694)	923.5(746)	S=O str

1.2 Binuclear molecules with one SO_2 ligand

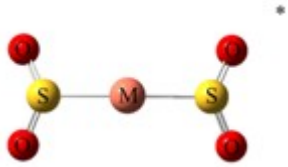
Table 3S: Calculated frequencies for the $M_2(\eta^1\text{-}SO_2)$ ($^1A'$) (M = Cu, Ag) and $Au_2(\eta^1\text{-}SO_2)$ (^1A) molecules



16-O	18-O	16-O/34-S	Mode assignment
	$Cu_2(\eta^1\text{-}SO_2)$		
513.8(66)	493.4 (59)	509.1(66)	O=S=O bend
1137.3(324)	1086.9(306)	1130.0 (314)	O=S=O str
1350.1(161)	1306.1(150)	1333.1(157)	O=S=O astr
	$Ag_2(\eta^1\text{-}SO_2)$		
511.9(64)	491.0 (57)	507.5(64)	O=S=O bend
1139.0(330)	1088.4(312)	1131.8(320)	O=S=O str
1350.4(163)	1306.4(153)	1333.4(159)	O=S=O astr
	$Au_2(\eta^1\text{-}SO_2)$		
512.7(50)	491.6(45)	508.4(50)	O=S=O bend
1134.2(341)	1083.8(321)	1126.9(332)	O=S=O str
1343.6(165)	1299.8 (154)	1326.7(161)	O=S=O astr

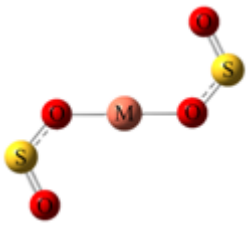
1.3 Mononuclear molecules with two SO_2 ligands

Table 4S: Calculated frequencies for the $M(\eta^1\text{-}SO_2)_2(^2A_1)$ (M = Cu, Ag) and $Au(\eta^1\text{-}SO_2)_2$ (^2A) molecules



16-O	18-O	16-O/34-S	Mode assignment
	$Cu(\eta^1\text{-}SO_2)_2$		
501.9(92)	483.0 (78)	497.0(94)	O=S=O bend
1069.4(1564)	1021.7(1458)	1062.6(1528)	O=S=O str
1334.4(305)	1291.0(285)	1317.6 (298)	O=S=O astr
	$Ag(\eta^1\text{-}SO_2)_2$		
499.0(117)	479.0 (102)	494.5(117)	O=S=O bend
1080.4(1452)	1031.7(1357)	1073.8(1417)	O=S=O str
1331.1(319)	1287.7(298)	1314.4(312)	O=S=O astr
	$Au(\eta^1\text{-}SO_2)_2$		
500.2(131)	479.9(114)	495.9(131)	O=S=O bend
1081.6(1724)	1032.9(1609)	1075.0(1683)	O=S=O str
1329.1(323)	1285.7 (301)	1312.4(315)	O=S=O astr

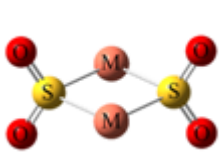
Table 5S: Calculated frequencies for the M(η^1-OSO)$_2$ (^2A_u) (M = Cu, Ag, Au) molecules



16-O	18-O	16-O/34-S	Mode assignment
	Cu(η^1-OSO)$_2$		
550.9(21)	525.5 (19)	549.9(21)	O=S=O bend
880.8(1925)	843.5(1773)	874.3(1892)	O=S=O str
1220.3(793)	1177.7(719)	1206.5(786)	O=S=O astr
	Ag(η^1-OSO)$_2$		
521.4(29)	498.0 (20)	518.1(32)	O=S=O bend
887.3(2409)	850.2(2219)	880.5(2366)	O=S=O str
1214.9(717)	1173.0(649)	1200.9(712)	O=S=O astr
	Au(η^1-OSO)$_2$		
509.7(91)	489.8(67)	504.8(98)	O=S=O bend
922.9(2623)	882.5(2420)	916.8(2574)	O=S=O str
1186.4(423)	1146.2 (390)	1172.3.(416)	O=S=O astr

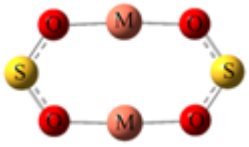
1.4 Dimer species

Table 6S: Calculated frequencies for the M$_2$(μ_2-SO$_2$)$_2$ (^1A_g) molecules (M= Cu, Ag, Au)



16-O	18-O	16-O/34-S	Mode assignment
	Cu$_2$(μ_2-SO$_2$)$_2$		
500.1(131)	480.0 (116)	495.6(130)	O=S=O bend
1095.5(599)	1046.9(568)	1088.4(580)	O=S=O str
1305.4(292)	1262.3(270)	1289.4(287)	O=S=O astr
	Ag$_2$(μ_2-SO$_2$)$_2$		
502.8(128)	482.4 (113)	498.3(128)	O=S=O bend
1097.3(648)	1048.8(613)	1090.3(629)	O=S=O str
1307.6(290)	1264.6(276)	1291.4(293)	O=S=O astr
	Au$_2$(μ_2-SO$_2$)$_2$		
499.8(118)	479.2(104)	495.5 (119)	O=S=O bend
1085.0(726)	1037.0(684)	1077.9(706)	O=S=O str
1294.6(303)	1251.8 (279)	1278.6(297)	O=S=O astr

Table 7S: Calculated frequencies for the $M_2(\eta^2\text{-}O_2S)_2$ ($^3B_{1u}$) molecules (M = Cu, Ag, Au)



16-O	18-O	16-O/34-S	Mode assignment
	$Cu_2(\eta^2\text{-}O_2S)_2$		
532.0(67)	506.0 (61)	531.9(68)	O=S=O bend
997.9(195)	956.4(180)	990.2(192)	O=S=O str
1026.0(394)	990.4(366)	1014.2(386)	O=S=O astr
	$Ag_2(\eta^2\text{-}O_2S)_2$		
495.2 (63)	469.6 (54)	494.1(65)	O=S=O bend
1001.2(238)	958.2(218)	992.6(236)	O=S=O str
1024.2(474)	989.8(438)	1012.0(465)	O=S=O astr
	$Au_2(\eta^2\text{-}O_2S)_2$		
477.1(56)	453.4(46)	475.2 (58)	O=S=O bend
1001.2(241)	959.2(220)	993.6(238)	O=S=O str
1029.4(511)	994.9 (472)	1016.9(502)	O=S=O astr

2. DFT calculations for the $Cu(\eta^2\text{-}O_2S)(\eta^1\text{-}Ar)$ molecule with the same method as described in the paper. Frequencies and intensities (in parentheses) are in cm^{-1} and km mol^{-1}.

Table 8S: Calculated frequencies for the $Cu(\eta^2\text{-}O_2S)(\eta^1\text{-}Ar)$ ($^2B_1$) molecule based on the B3LYP functional.

16-O	18-O	16-O/34-S	Mode assignment
6.0(0)	5.2(0)	5.3(0)	$Cu(\eta^2\text{-}O_2S)(\eta^1\text{-}Ar)$ def
47.1(0)	47.1(0)	46.8(0)	Ar-Cu-S bend
131.0(0)	130.3(0)	130.6(0)	Cu-Ar str
175.6(2)	166.2(2)	175.6(2)	$Cu(\eta^2\text{-}O_2S)$ def
184.6(14)	177.4(13)	183.2(14)	$Cu(\eta^2\text{-}O_2S)$ def
301.5(28)	298.3(28)	298.9(27)	$Cu(\eta^2\text{-}O_2S)$ def
554.1(39)	527.4(33)	551.6(40)	O=S=O bend
983.0(75)	943.5(70)	974.7(74)	O=S=O str
998.6(202)	963.7(187)	987.3(199)	O=S=O astr

Table 9S: Calculated frequencies for the Cu(η^2-O_2S)(η^1-Ar) ($^2A''$) molecule based on the BPW91 functional.

16-O	18-O	16-O/34-S	Mode assignment
42.6(1)	42.4(1)	42.4(1)	Cu(η^2-O_2S)(η^1-Ar) def
61.0(0)	60.6(0)	60.6(0)	Cu(η^2-O_2S)(η^1-Ar) def
118.0(10)	112.4(10)	117.9(10)	Cu(η^2-O_2S) def
157.8(0)	157.0(0)	157.4(0)	Cu-Ar str
159.0(10)	152.8(9)	158.0(10)	Cu(η^2-O_2S) def
330.9(10)	325.7(11)	328.0(9)	Cu(η^2-O_2S) def
531.0(26)	505.0(22)	529.4(27)	O=S=O bend
888.6(109)	854.8(98)	880.0(109)	S=O str
984.8(110)	948.4(104)	974.8(106)	S=O str

3. The spectra for gold atom reactions with SO_2 in solid neon with varied laser energy.

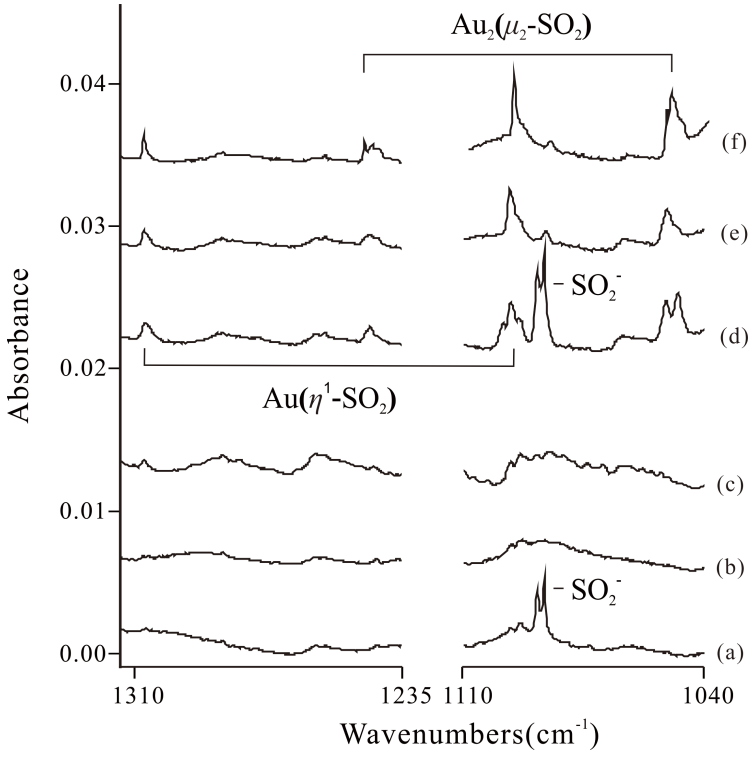


Fig.1S. (a) Au + SO_2 deposition for 60 min(0.2% in Ne matrix gas, ~10mJ/pulse); (b) after full-arc irradiation; (c) after annealing to 10 K; (d) Au + SO_2 deposition for 60 min(0.2% in Ne matrix gas, ~20mJ/pulse); (e) after full-arc irradiation; (f) after annealing to 10 K.