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Citation: The Journal of Chemical Physics **120**, 5717 (2004); doi: 10.1063/1.1648634 View online: http://dx.doi.org/10.1063/1.1648634 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/120/12?ver=pdfcov Published by the AIP Publishing

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Isomers of HSCO: IR absorption spectra of *t*-HSCO in solid Ar

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(Received 10 December 2003; accepted 24 December 2003)

Irradiation of an Ar matrix sample containing H₂S and CO (or OCS) with an ArF excimer laser at 193 nm yields *trans*-HSCO (denoted *t*-HSCO). New lines at 1823.3, 931.6, and 553.3 cm⁻¹ appear after photolysis and their intensity enhances after annealing; secondary photolysis at 248 nm diminishes these lines and produces OCS and CO. These lines are assigned to C–O stretching, HSC-bending, and C–S stretching modes of *t*-HSCO, respectively, based on results of ¹³C-isotopic experiments and theoretical calculations. Theoretical calculations using density-functional theories (B3LYP and PW91PW91) predict four stable isomers of HSCO: *t*-HSCO, *c*-HSCO, HC(O)S, and *c*-HOCS, listed in increasing order of energy. According to calculations with B3LYP/aug-cc-pVTZ, *t*-HSCO is planar, with bond lengths of 1.34 Å (H–S), 1.81 Å (S–C), and 1.17 Å (C–O), and angles \angle HSC=93.4° and \angle SCO=128.3°; it is more stable than *c*-HSCO and HC(O)S by ~9 kJ mol⁻¹ and more stable than *c*-HOCS by ~65 kJ mol⁻¹. Calculated vibrational wave numbers, IR intensities, and ¹³C-isotopic shifts for *t*-HSCO fit satisfactorily with experimental results. This new spectral identification of *t*-HSCO provides information for future investigations of its roles in atmospheric chemistry. © 2004 American Institute of Physics. [DOI: 10.1063/1.1648634]

I. INTRODUCTION

Sulfate aerosol, typically produced from the oxidation of SO₂ in the atmosphere, scatters and absorbs radiation from the Sun; it also plays an important role in heterogeneous reactions in the atmosphere.^{1,2} In the stratosphere, SO₂ is either injected directly from eruptions of volcanoes, or produced via oxidation of sulfur compounds. Hydrogen sulfide (H₂S) is an important anthropogenic source of reduced sulfur compounds that lead to formation of SO₂ in the atmosphere; current estimates of its annual loading are 1–3 Tg yr⁻¹ of sulfur;³ 1 Tg=10¹² g. Atmospheric oxidation of H₂S is initiated through its reaction with OH to produce HS radical.^{4,5} Subsequent reactions of HS with O₃ and NO₂ produce HSO, which reacts further with O₃ and NO₂ to form HSO₂.^{5,6} The hydrogen atom of HSO₂ is rapidly abstracted by O₂, yielding SO₂.

Alternative paths for oxidation of HS that might be important in the atmosphere have been investigated. Reaction of HS with CO in air might yield carbonyl sulfide (OCS);⁷ this reaction is analogous to reaction of OH with CO that yields CO_2 . If this reaction is important, it provides a pathway to convert H₂S to OCS; current estimates of atmospheric sources of OCS would consequently have to be revised.⁸

Unlike the exothermic reaction of OH with CO,

$$OH+CO \rightarrow H+OCO, \quad \Delta H^0 = -104 \text{ kJ mol}^{-1}, \qquad (1)$$

the reaction of HS with CO to give OCS and H,

$$HS+CO \rightarrow H+OCS, \quad \Delta H^0 = 51 \text{ kJ mol}^{-1},$$
 (2)

is endothermic and is expected to be unimportant in the atmosphere.⁹ However, if the adduct HSCO were formed to some extent via the equilibrium reaction,

$$HS+CO \leftrightarrow HSCO, \Delta H^0 \cong 2 \text{ kJ mol}^{-1},$$
 (3)

a subsequent reaction of HSCO with O₂,

$$HSCO + O_2 \rightarrow HO_2 + OCS, \quad \Delta H^0 \cong -163 \text{ kJ mol}^{-1}$$
(4)

might produce HO₂ and OCS with great exothermicity. The energy of HSCO in *trans* form (denoted as *t*-HSCO) is predicted to be similar to that of reactants HS and CO, and a small barrier (14 kJ mol^{-1}) for formation of *t*-HSCO from HS and CO is predicted.^{10,11} To our knowledge, no spectral information on HSCO exists.

The matrix isolation technique is known for its superiority in trapping and preserving unstable species.^{12,13} Photofragments produced upon photolysis of a matrix sample are likely to be confined within a matrix cage and to react with each other because of the cage effect; the possibility to form various isomers of the precursor or other products from secondary reactions is hence much greater than in the gaseous phase. Selective photodissociation with a laser avoids secondary photolysis on species of interest. Using various lasers

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to photodissociate matrix samples, we produced numerous novel species that are difficult to form in the gaseous phase.^{14–27} Here we report a theoretical investigation of possible isomers of HSCO and experimental production of *t*-HSCO, by irradiation of matrix-isolated H₂S and CO or OCS with laser emission at 193 nm, and its infrared identification.

II. EXPERIMENTS

The experimental setup is similar to that described previously.^{15,19} A copper plate coated with platinum and cooled to ~13 K serves as a substrate for a cold matrix sample and as a mirror to reflect incident infrared (IR) beam to the detector. Gaseous mixtures of H₂S/Ar (typically in proportions 1/200) and CO/Ar (or OCS/Ar, typically 1/400) were codeposited. Typically 10 mmol of a sample mixture was deposited over a period of 2 h.

IR absorption spectra were recorded with an evacuable Fourier-transform infrared (FTIR) spectrometer (Bomem, DA8) equipped with a KBr beamsplitter and a Hg/Cd/Te detector (cooled to 77 K) to cover the spectral range 500–4000 cm⁻¹. Typically 600 scans with resolution of 0.5 cm⁻¹ were recorded at each stage of the experiment.

An ArF excimer laser (193 nm), operated at 10 Hz with energy ~ 4 mJ pulse⁻¹, was employed to photodissociate H₂S. A KrF excimer laser (248 nm), operated at 10 Hz with energies ~ 4 mJ pulse⁻¹, was used for secondary photolysis.

 H_2S (>99.5%, Scott Specialty Gases), CO (99.9%, Air Products), OCS (99.98%, Scientific Gas Products), ¹³CO and O ¹³CS (both from Cambridge Isotope Laboratories, isotopic purity >99%) were used without further purification except for degassing at 77 K. Ar (99.999%, Scott Specialty Gases) was used without purification.

III. COMPUTATIONAL METHOD

The equilibrium structure, vibrational frequencies, IR intensities, and energies were calculated with the GAUSSIAN 98 program.²⁸ We used density functional theory (DFT) in calculations of two types, B3LYP and PW91PW91: the B3LYP method uses Becke's three-parameter hybrid exchange functional,²⁹ and a correlation functional of Lee, Yang, and Parr,^{30,31} with both local and nonlocal terms; the PW91PW91 method uses exchange and correlation functionals of Perdew and Wang.^{32,33} Dunning's correlation-consistent polarized valence triplet-zeta basis set, augmented with *s*, *p*, *d*, and *f* functions (aug-cc-pVTZ), were used in all methods. Analytic first derivatives were utilized in geometry optimization, and vibrational frequencies were calculated analytically at each stationary point.

IV. RESULTS AND DISCUSSION

A. Experimental observations and assignments

1. Experiments with H₂S and CO in natural abundance

The IR spectrum of H_2S for a sample of $H_2S/CO/Ar$ (2/1/800) at 13 K exhibits multiple lines due to rotation and aggregation; observed lines of asymmetric H–S stretching (ν_3) at 2648.0, symmetric H–S stretching (ν_1) at 2629.8

cm⁻¹ and HSH bending (ν_2) at 1180.1 cm⁻¹ are consistent with a previous report (maxima at 2647.8, 2630.0, and 1180.0 cm⁻¹ in solid Ar).³⁴ Lines at 2581.8 and 2577.6 cm⁻¹ are due to dimer and trimer of H₂S, respectively. A line at 2585.5 cm⁻¹ was assigned to a complex of H₂S and H₂O.³⁴ The IR spectrum of CO ~2138.2 cm⁻¹ is broad and a weaker line at 2149.3 cm⁻¹ is due to a complex of CO and H₂O.³⁵ Infrared absorption of the H₂S·CO complex was studied by Lundell *et al.*,³⁶ but we found no absorption with wave numbers 2637.3, 2611.4, 2597.5, 2143.0, and 2137.4 cm⁻¹ reported by them.

Partial spectra of a H₂S/CO/Ar (2/1/800) matrix sample in regions 525-600, 920-980, 1800-2200, and 2540-2660 cm^{-1} before and after laser irradiation are shown in Fig. 1. Trace A is the spectrum recorded after deposition, and traces B is a difference spectrum after irradiation at 193 nm for 10 min. The difference spectrum was derived on subtracting the spectrum recorded in the preceding stage of irradiation/ annealing from a new spectrum; a positive feature indicates production, whereas a negative feature indicates destruction. After irradiation, lines at 2049.7, 858.5, and 520.0 cm^{-1} are readily assigned to OCS, consistent with literature values of OCS in the gas phase³⁷ or in matrices.²⁵ Lines at 2481.4, 1863.6, and 1085.6 cm^{-1} are readily assigned to HCO, consistent with literature values of 2483, 1863, and 1087 cm⁻¹ for HCO in solid Ar.³⁸ Weak lines at 3602.9, 1843.7, 1211.0, and 1064.2 cm⁻¹ are due to *t*-HOCO.³⁹ Intensities of new lines at 1823.3, 931.6, and 553.3 cm^{-1} (marked as • in Fig. 1) increased slightly upon further irradiation of the sample and increased substantially after the temperature of the matrix was raised to \sim 30 K for 10 min, whereas those of other lines remained nearly invariant, as shown in the difference spectrum in trace C of Fig. 1. Weaker lines at 930.2 and 551.4 cm^{-1} are due to site splitting from lines at 931.6 and 553.3 cm^{-1} , respectively. Further irradiation of the matrix sample with laser emission at 248 nm for 10 min diminished these new lines nearly completely, whereas intensities of lines due to OCS, and CO to a less extent, were recovered, as illustrated in the difference spectrum in trace D of Fig. 1. Line positions of reactants and products are listed in Table I.

Similar experiments were performed with a matrix sample of $H_2S/OCS/Ar$ (2/1/800), but the spectra appeared to be more complex than those recorded for $H_2S/CO/Ar$ experiments. Nevertheless, after irradiation at 193 nm, the three new lines at 553.3, 931.6, and 1823.3 cm⁻¹ were also observed.

2. ¹³C-isotopic experiments and assignments

An isotopic mixture containing ¹³CO and ¹²CO in nearly equal proportion was used in one experiment. A difference spectrum after irradiation of this matrix sample at 193 nm for 10 min, followed by annealing at 30 K is shown in trace B of Fig. 2; trace A depicts the corresponding difference spectrum of a natural H₂S/CO/Ar matrix sample after irradiation and annealing for comparison. Line positions of ¹³C-substituted species are listed parenthetically in Table I.

The line at 1823.3 cm⁻¹ splits into two lines, with a new line at 1784.7 cm⁻¹ having a smaller intensity. Part of the intensity of the line at 1823.3 cm⁻¹ might be contributed by



FIG. 1. Partial IR absorption spectrum of a $H_2S/CO/Ar$ (2/1/800) matrix sample before irradiation (A), difference spectrum after irradiation at 193 nm for 10 min (B), difference spectrum after annealing of the matrix sample at 30 K for 10 min (C), and difference spectrum after further irradiation of the matrix at 248 nm for 10 min (D).

H ¹³CO that absorbs at the same wave number. The isotopic pattern indicates that one C atom is involved in this mode. The isotopic ratio 1784.7/1823.3=0.9788, defined as a ratio of vibrational wave numbers of the isotopically labeled species to that of the most naturally abundant species, is similar to the theoretical value of 0.9778 for CO. The line at 553.3 cm⁻¹ splits into two lines with approximately equal intensity, with the new line at 537.8 cm⁻¹; the ¹³C-isotopic ratio of 537.8/553.3=0.9720 is near a theoretical value of 0.9716 for CS. The doublet line at 931.6 and 930.2 cm⁻¹, with the latter

TABLE I. Wave numbers (in cm^{-1}) of lines observed for a H₂S/CO/Ar matrix sample after deposition and after irradiation at 193 nm.

After deposition	After irradiation ^a	Assignment		
2648.0		H_2S , asym. stretch (ν_3)		
2629.8		H_2S , sym. stretch (ν_1)		
1180.1		H_2S , bend (ν_2)		
2585.5		$H_2S \cdot H_2O$		
2581.8		(H ₂ S) ₂		
2577.6		$(H_2S)_3$		
2568.8		$(H_2S)_n$?		
2149.3 (2101.9) ^b		$CO \cdot H_2O$		
2138.2 (2091.1)		CO		
	1823.3(1784.7) ^b	<i>t</i> -HSCO, C–O stretch (ν_2)		
	931.6(930.2)	<i>t</i> -HSCO, HSC-bend (ν_3)		
	553.3(537.8)	<i>t</i> -HSCO, C–S stretch (ν_4)		
	2481.4(2475.5)	HCO, C–H stretch (ν_1)		
	1863.6(1823.3)	HCO, C–O stretch (ν_3)		
	1085.6(1079.3)	HCO, bend (ν_2)		
	3602.9	<i>t</i> -HOCO, O–H stretch (ν_1)		
	1843.7	<i>t</i> -HOCO, C–O stretch (ν_2)		
	1211.0	<i>t</i> -HOCO, HOC-bend (ν_3)		
	1064.8	<i>t</i> -HOCO, C–O stretch (ν_4)		

^aPhotolysis at 193 nm for 10 min.

^bNumbers listed in parentheses correspond to ¹³C species.

associated with a minor site, shifts to 930.2 and 928.8 cm⁻¹, respectively; the spectrum hence appears as a triplet. The small ¹³C-isotopic shift for the line at 931.6 cm⁻¹ indicates that it might be associated with either a bending mode or a mode not directly involving the C atom.

A second isotopic sample containing equimolar O 13 CS and O 12 CS in Ar was also used. Isotopically shifted lines at 1784.7, 930.2, and 537.8 cm⁻¹ were also observed. A detailed discussion of other reaction products of experiments on H₂S/OCS/Ar matrix samples will be reported elsewhere.

Photodissociation of H_2S at 193 nm forms H and HS.⁴⁰ Annealing of the matrix sample is expected to promote diffusion, hence reaction between CO and HS (or H); in addition to HCO, isomers of HSCO are expected to be formed.



FIG. 2. Partial difference IR absorption spectra of $H_2S/CO/Ar$ matrix samples with isotopic variants after irradiation at 193 nm for 10 min followed by annealing at 30 K for 10 min. (A) $H_2S/{}^{12}CO/Ar$ (2/1/800) and (B) $H_2S/{}^{13}CO/{}^{12}CO/Ar$ (2/1/1/800).

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FIG. 3. Geometries and relative energies (in kJ mol⁻¹) of isomers of HSCO calculated with B3LYP/aug-cc-pVTZ and PW91PW91/aug-cc-pVTZ methods. Relative energies are corrected with zero-point energies; unit of bond length is Å. Results from PW91PW91 are listed in parentheses.

Because observed isotopic shifts indicate that the species contains a C–O bond and a C–S bond, and because observed C–S stretching wave numbers shifted substantially from 860 cm⁻¹ of OCS to 553 cm⁻¹, whereas observed C–O stretching wave numbers shifted only from 2049 cm⁻¹ of OCS to 1823 cm⁻¹, the new species is likely HSCO rather than HOCS or HC(O)S. With experimental data alone, we are unable to identify unambiguously whether the observed species has *trans* or *cis* conformation, but the conformation may be determined by comparison with theoretical calculations.

B. Comparison with theoretical calculations

We performed theoretical calculations using B3LYP and PW91PW91 methods, both with aug-cc-pVTZ basis sets, to find four stable isomers of HSCO: *t*-HSCO, *c*-HSCO, HC(O)S, and *c*-HOCS. Geometries and energies predicted

for these species are shown in Fig. 3, with those predicted using PW91PW91 listed in parentheses. The most stable species is *t*-HSCO, but *c*-HSCO and HC(O)S have energies greater by only ~9 kJ mol⁻¹. The isomer *c*-HOCS, lying 65 kJ mol⁻¹ above *t*-HSCO, is the highest in energy. The PW91PW91 method predicts a similar trend with slightly smaller energy gaps. The energies and structures predicted in this work are close to those predicted previously with QCISD(T) and other methods, but a fifth isomer *t*-HOCS was predicted to be stable, with energy ~2 kJ mol⁻¹ below *c*-HOCS.¹¹

Both conformers of HSCO are characterized by a short C–O bond (~1.17 Å) similar to a double bond (cf. 1.15 Å for OCS) and a C–S bond with single-bond character; the C–S bond length (1.812 Å) of *t*-HSCO is slightly greater than that of *c*-HSCO (1.787 Å). In contrast, *c*-HOCS is characterized by a short C–S bond of length 1.59 Å and a long C–O bond, 1.30 Å. HC(O)S has a C–S bond of length similar to that in *t*-HSCO, but a C–O bond of length between those of *t*-HSCO and *c*-HOCS.

Tables II and III list vibrational wave numbers, approximate mode description, and infrared intensities (in parentheses) of four isomers of HSCO predicted with B3LYP and PW91PW91 methods. Trend of stretching vibrational wave numbers reflect the bond lengths discussed above, with wave numbers of C–O stretching modes, predicted with B3LYP/ aug-cc-pVTZ, decreasing from 1881 cm⁻¹ for *t*-HSCO, 1864 cm⁻¹ for *c*-HSCO, 1699 cm⁻¹ for HC(O)S, to 1418 cm⁻¹ for *c*-HOCS. In contrast, wave numbers of C–S stretching predicted with B3LYP increase from 480 cm⁻¹ for *c*-HSCO, 553 cm⁻¹ for *t*-HSCO, 681 cm⁻¹ for HC(O)S, to 887 cm⁻¹ for *c*-HOCS.

Observed vibrational wave numbers of new lines at 1823.3, 931.6, and 553.3 cm⁻¹ are near values predicted for ν_2 (C–O stretching), ν_3 (HSC-bending), and ν_4 (C–S stretching) modes of *t*-HSCO. The experimental ν_2 value is nearer the value of 1816 cm⁻¹ predicted with the PW91PW91 method than the value of 1881 cm⁻¹ predicted with the B3LYP method, whereas the experimental ν_4 value is closer to the value of 553 cm⁻¹ predicted with the B3LYP method than the value of 573 cm⁻¹ predicted with the

TABLE II. Vibrational wave numbers (in cm^{-1}) and infrared intensities of *t*-HSCO and *c*-HSCO predicted with two DFT methods.

Species	Vibrational mode	B3LYP/ aug-cc-pVTZ	PW91PW91/ aug-cc-pVTZ	Experiment Ar matrix
t-HSCO	ν_1 , H–S stretch	2696.3 (2) ^a	2634.4 (3) ^a	
	ν_2 , C–O stretch	1881.3 (417)	1816.4 (372)	1823.3
	ν_3 , HSC-bend	947.8 (35)	922.8 (32)	931.6
	ν_4 , C–S stretch	552.7 (60)	572.7 (53)	553.3
	ν_5 , out-of-plane bend	392.0 (7)	404.0 (8)	
	ν_6 , SCO-bend	369.1 (12)	371.0 (7)	
c-HSCO	ν_1 , H–S stretch	2589.1 (0.4)	2506.3 (2)	
	ν_2 , C–O stretch	1864.0 (357)	1800.7 (319)	
	ν_3 , HSC-bend	872.4 (35)	839.4 (36)	
	ν_4 , C–S stretch	479.9 (65)	485.9 (44)	
	ν_5 , out-of-plane bend	412.9 (10)	413.9 (9)	
	ν_6 , SCO-bend	386.4 (3)	369.2 (6)	

^aIR intensities (in km mol⁻¹) are listed in parentheses.

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TABLE III. Vibrational wave numbers (in cm^{-1}) and infrared intensities of HC(O)S and *c*-HOCS predicted with two DFT methods.

Species	Vibrational mode	B3LYP/ aug-cc-pVTZ	PW91PW91/ aug-cc-pVTZ
HC(O)S	ν_1 , C–H stretch	2934.8 (69) ^a	2941.5 (58) ^a
	ν_2 , C–O stretch	1699.1 (277)	1536.2 (54)
	ν_3 , HCO bend	1339.4 (14)	1265.5 (11)
	ν_4 , out-of-plane bend	927.6 (4)	894.1 (7)
	ν_5 , C–S stretch	681.1 (131)	798.4 (77)
	ν_6 , OCS bend	232.5 (31)	354.5 (25)
c-HOCS	ν_1 , O–H stretch	3516.8 (9)	3342.1 (19)
	ν_2 , C–O stretch	1417.6 (396)	1399.8 (320)
	ν_3 , HOC bend	1243.7 (151)	1199.8 (130)
	ν_4 , C–S stretch (mixed)	886.7 (7)	859.0 (9)
	ν_5 , out-of-plane bend	587.3 (72)	580.1 (62)
	ν_6 , OCS bend	436.5 (12)	420.3 (10)

^aIR intensities (in km mol⁻¹) are listed in parentheses.

PW91PW91 method. The ν_2 values, 1864 and 1801 cm⁻¹ predicted with B3LYP and PW91PW91, respectively, for *c*-HSCO are also near the experimental observation, but predicted ν_3 (872 and 839 cm⁻¹) and ν_4 (480 and 486 cm⁻¹) are smaller than those from experiments by more than 6% and 12%, respectively. The observed ratio of integrated intensities for $\nu_2:\nu_3:\nu_4$, 1.00:0.06:0.08, agrees satisfactorily with the ratio 1.00:0.08:0.14 predicted for *t*-HSCO with the B3LYP method.

Table IV lists predicted ¹³C-isotopic ratios of four isomers. As both B3LYP and PW91PW91 methods predict nearly identical isotopic ratios, only those predicted with B3LYP are listed. Predicted isotopic ratios for *t*-HSCO are nearly the same as those determined experimentally (deviations <0.0018); ratios predicted for other isomers of HSCO fit less well with experimental results. *Hence, based on observed* ¹³C-*isotopic shifts and comparison with vibrational wave numbers and isotopic ratios predicted with theoretical calculations, we conclude that new absorption lines at 1823.3, 931.6, and 553.3 cm⁻¹ are associated with* ν_2 , ν_3 , *and* ν_4 *vibrational modes of t-HSCO isolated in solid Ar.*

C. Mechanism of formation of t-HSCO

Photolysis of H_2S at 193 nm produced H atom and HS radical;⁴⁰ observation of absorption lines of HCO at 2481.4, 1863.6, and 1085.6 cm⁻¹ indicates that some H atoms react with CO to form HCO. Formation of OCS is likely due to reactions of CO with S or HS. That annealing of the matrix

TABLE IV. Experimental and calculated ¹³C-isotopic ratios^a of four isomers of HSCO.

Species	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Experiment		0.9788	0.9985	0.9720		
t-HSCO	0.9999	0.9782	0.9983	0.9701	0.9911	0.9935
c-HSCO	0.9999	0.9783	0.9928	0.9781	0.9903	0.9904
HC(O)S	0.9971	0.9793	0.9952	0.9866	0.9777	0.9938
c-HOCS	0.9998	0.9723	0.9936	0.9861	0.9913	0.9856

^aDefined as the ratio of vibrational wave numbers of a ¹³C isotopomer to that of the corresponding ¹²C species.

at 30 K produced t-HSCO in substantial amount but much less HCO indicates that H atom might have been depleted before annealing and that formation of HSCO involves diffusion of either HS or CO. The reaction for association of HS and CO to form t-HSCO [reaction (3)] is predicted at the QCISD//UMP2/6-311+G(2df,2p) level to be slightly endothermic ($\Delta H^0 \cong 2.5 \text{ kJ mol}^{-1}$) with a small (14 kJ mol⁻¹) barrier,¹¹ but this reaction was predicted to be exothermic by 13-33 kJ mol⁻¹ with a barrier of 2-7 kJ mol⁻¹ at MP2. B3LYP, and BLYP level.¹¹ Our observation of *t*-HSCO upon annealing of the matrix at 30 K indicates that the barrier, if it exists, would be small and the reaction should be nearly thermal neutral or exothermic. A small loss of OCS upon annealing indicates that the reaction of H+OCS might also take place, but theoretical calculations predict a barrier >28kJ mol⁻¹ for the reaction of H and OCS to form *c*-HSCO.

When the 193-nm irradiated $H_2S/CO/Ar$ sample was irradiated further at 248 nm, lines due to *t*-HSCO disappeared, whereas lines due to OCS increased and the line due to CO increased slightly. This observation indicates that at 248 nm *t*-HSCO is photodissociated to form mainly OCS; OCS further dissociates at 248 nm and the fragments might escape from the cage to form CO and S.⁴¹ Further investigations of electronic absorption spectra of *t*-HSCO are needed to understand its photolytic behavior.

On the basis of spectral information of *t*-HSCO obtained in this work, further experiments in the gaseous phase at low temperatures might be performed to investigate the adduct formation and equilibrium of reaction (3) to assess the importance of this reaction in atmospheric chemistry. Even if only 4% of HS be converted to OCS via *t*-HSCO under atmospheric conditions, it contributes about 50% of the estimated total source of OCS into the atmosphere.^{3,8}

V. CONCLUSION

We irradiated matrix samples of H₂S/CO/Ar and H₂S/OCS/Ar with an ArF excimer laser at 193 nm and observed new IR absorption lines at 1823.3, 931.6, and 553.4 cm⁻¹. These new features are attributed to C–O stretching (ν_2), HSC-bending (ν_3), and C–S stretching (ν_4) modes of

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to TP 130.88.90.140 On: Mon. 08 Dec 2014 12:47:33 *t*-HSCO, respectively, based on observed ¹³C-isotopic shifts and theoretical predictions of line positions, infrared intensities, and ¹³C/¹²C isotopic ratios for possible isomers of HSCO. According to calculations *t*-HSCO has energy smaller than that of isomers *c*-HSCO, HC(O)S, and *c*-HOCS. The product *t*-HSCO was formed mainly via reaction of HS and CO in the matrix; secondary photolysis at 248 nm depleted *t*-HSCO and produced mainly OCS. This work provides spectral information for future investigations of atmospheric reaction of HS+CO using IR detection of *t*-HSCO; formation of HSCO may have significant implication for atmospheric chemistry.

ACKNOWLEDGMENTS

We thank A. R. Ravishankara for bringing to our attention the importance of the reaction of HS and CO in the atmosphere, and the National Science Council of Taiwan (Grant No. NSC92-2113-M-007-033) and MOE Program for Promoting Academic Excellence of Universities (Grant No. 89-FA04-AA) for support. W.J.L. thanks the Institute of Atomic and Molecular Sciences, Academia Sinica for a short-term visiting professorship.

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