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Chemiluminescent reactions of sulfur atoms and oxygen atoms in solid argon matrices. SO chemiluminescence

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When dilute argon matrices containing H_2S+O_3 , $OCS+O_3$ and H_2S+NO_2 molecules are exposed to ultraviolet radiation and subsequently allowed to warm from 8 to ~ 20 °K, several intense visible emissions with extensive vibrational structure appear. Besides those emissions of O2, S2, and SO2, two new luminescent systems are evident. Extensive oxygen-18 and deuterium isotopic studies demonstrated the absence of hydrogen and the presence of a single oxygen atom in the emitting species of both systems, while matrix concentration studies established that the excited state species was an intermediate in SO2 formation, presumably molecular SO. The more intense of the two systems is located between 490-870 nm and contains up to ten members. The low values calculated for $T_0 = 22543$ cm⁻¹ and $\omega_e = 1130.7$ cm⁻¹ suggest that this transition is most likely SO ($c^{1}\Sigma^{-} \rightarrow a^{1}\Delta$). A second, weaker emission system of SO with approximately eight members was found between 385-600 nm. T_0 for this latter system was estimated at 28400 ± 1150 cm⁻¹, the larger uncertainty being due to the weakness of the system and overlap with SO_2 chemiluminescence. The magnitude of T_0 , as well as the value calculated for $\omega_e^{-} = 1157.9 \text{ cm}^{-1}$, is consistent with the assignment of this transition to the SO(A'³ $\Delta \rightarrow X$ ³ Σ^{-}) system which has recently been reported for S_2 and O_2 chemiluminescence. Ground state oxygen atoms $O({}^{3}P)$ were observed to react with H₂S in cryogenic matrices to produce only SO₂ chemiluminescence, while no emissions were observed in similar experiments with OCS.

INTRODUCTION

Recently, several cases of visible-ultraviolet luminescence appearing upon warmup of solid cryogenic matrices containing traces of highly reactive species (viz., atoms) have been reported.¹⁻⁸ Sulfur atoms have been observed^{3, 5, 8} to recombine in solid argon at 10-30°K to produce intense chemiluminescence in the 365-555 nm spectral region assignable to the $B^{3}\Sigma_{u}^{-} + X^{3}\Sigma_{s}^{-}$ emission system of S₂. The analogous oxygen atom recombination reaction, on the other hand, is not exothermic enough to populate the $B^{3}\Sigma_{u}^{-}$ state, although emissions of O₂ have been observed in the 350-675 nm spectral region.^{8, 9} In the case of triatomics, the matrix reactions of sulfur atoms and oxygen molecules have been shown to produce the well known matrix phosphorescence spectrum of SO₂($a^{3}B_{1} + X^{1}A_{1}$).²⁻⁶

The present study reports two previously unknown luminescent systems which are observed upon annealing argon matrices containing traces of atomic sulfur and atomic oxygen. Our interest in this system was originally provoked by the observation⁸ of two unidentified chemiluminescent systems which appeared upon warmup of dilute, uv-photolyzed argon matrices initially containing $O_3 + H_2S$ molecules. The similarity of the experimentally determined spacings in these two systems $(\sim 1040 \text{ cm}^{-1})$ to the ground state vibrational spacings of the SO molecule $(\omega_{e} \sim 1148 \text{ cm}^{-1})^{10}$ compelled us to consider it as a likely emitter. Consequently, we report herein the results of an optical multichannel spectroscopic investigation of the luminescence observed upon controlled warmup of various selectively photolyzed argon matrices containing $H_2S + O_3$, $OCS + O_3$, and H_2S + NO₂ molecules. Subsequent experiments were conducted with oxygen-18- and deuterium-labeled reactants in an effort to identify the emitting species.

EXPERIMENTAL

Gaseous hydrogen sulfide (Matheson, 99.5% minimum purity) and D_2S (Merck and Co. Isotopes, 98 at. % D) were degassed at 77°K and used in a passivated stainless steel/Teflon vacuum manifold.⁶ OCS (Matheson) was condensed and degassed at 77°K prior to use. Ozone was prepared by the high voltage discharge of oxygen (Matheson, 99.6%) in a liquid-nitrogen-cooled Pyrex U tube connected to the vacuum manifold. Any unconverted O₂ was pumped away from the ozone condensate. Oxygen-18-enriched ozone was similarly prepared from ${}^{18}O_2$ (Miles Laboratories, Inc., 99.9 at. % ${}^{18}O$). Partially ${}^{18}O$ -enriched ozone was prepared by mixing appropriate amounts of ${}^{16}O_2$ and ${}^{18}O_2$ prior to ozone production. NO₂ (Matheson, 99%) was degassed at 195°K prior to use. N¹⁸O₂ (Miles Laboratories, Inc., 75 at. % ¹⁸O) was used without further purification. In one experiment, a 40% oxygen-18-enriched NO₂ sample was prepared by mixing appropriate amounts of natural and 75% oxygen-18-enriched NO₂. Argon (Linde, prepurified, 99.998%) was used as the matrix gas in this investigation and, in every case, was stored at ~20 psi prior to sample preparation in an effort to minimize contamination.

In all experiments to be described, matrix samples were deposited at 2-4 mmole/h for several hours onto a highly polished copper block which was maintained at a temperature near 8° K. After complete deposition, the samples were subsequently irradiated with either a high pressure mercury arc (Philips HPK 125 W) employing all-quartz optics and a 5 cm water filter, or with a helium-neon laser (Spectra-Physics model 125). Photolysis was usually performed for ~2 h with no detectable change in matrix temperature from either excitation source.

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At the conclusion of the photolysis periods, the copper block was temperature cycled several times to successively higher temperatures by interruption of the cryogenic helium compressor (Air Products Displex model CSW-202). Temperature changes in the $0-40^{\circ}$ K region were monitored with a chromel vs Au-0.07 at. %Fe thermocouple embedded in the copper block.

As described in a previous publication, ⁸ an optical multichannel analyzer (OMA) detection system was used to record the visible and near ultraviolet emissions which occurred during each matrix warmup cycle. Moreover, in every experiment described here, a redenhanced, image-intensified silicon target tube (ISIT) was employed as the primary photodetector. Sample spectra were calibrated in situ by a superposition of emissions from either a low pressure mercury pen lamp or a neon discharge bulb. Wavelength reproducibility was estimated to be within ± 0.5 nm (± 31.5 cm⁻¹ at 400 nm and ± 8 cm⁻¹ at 800 nm), which is believed to be the upper error limit in all reported frequencies.

One advantage of an OMA-based detection system in such a situation is the ability to observe, in real time, the growth and disappearance of several luminescent systems simultaneously during the course of the various matrix diffusion reactions. This capability was extended to several experiments where interference from overlapping SO_2 emissions (350-500 nm) was minimized by subtracting from those spectra recorded in initial warmups (where the relative SO_2 emission intensity is reduced although significant) the digitized spectra of later warmups in which SO_2 becomes the dominant emitting species.

RESULTS

An earlier publication from this laboratory⁸ first reported two new chemiluminescent systems (in addition to SO₂ phosphorescence) which were observed upon warmup of mercury-arc-photolyzed argon matrices containing traces of H₂S and ozone. These systems, which

EMISSION INTENSITY RELATIVE 400 480 560 640 $\lambda(nm)$ FIG. 1. Chemiluminescent emissions observed upon warmup

 $(8 \rightarrow 14 \text{ }^\circ\text{K})$ of a matrix sample codeposited at $8 \text{ }^\circ\text{K}$ from separate $Ar/O_3 = 100$ and $Ar/H_2S = 100$ mixtures, followed by 15 min of mercury-arc photolysis. $Ar/O_3/H_2S = 238/1.4/1.0$; 92 µmoles H₂S.

were simply labelled "B" and "C," are illustrated in Fig. 1. The object of the present investigation was to identify the species and the electronic transitions involved in these emission systems.

Visible light photolysis

Several argon matrices containing H₂S + O₃ molecules were photolyzed for periods of 2-4 h with the radiation from a helium-neon laser (75 mW, 632.8 nm) whose beam was expanded by $5 \times$ in order to illuminate the sample area. This excitation source has been recently demonstrated to be quite effective in photolyzing argonmatrix-isolated ozone.¹¹ The emissions observed upon sample warmup were attributable solely to SO₂ phosphorescence $(a \rightarrow X)$. Similar experiments using OCS instead of H₂S produced virtually no chemiluminescence. Consequently, we conclude that the two new luminescent systems are not attributable to an O-atom reaction with H₂S or OCS since 632.8 nm light is capable of photolyzing ozone (to produce O atoms) but not H₂S or OCS.

Other reagents

When argon matrices containing D₂S and O₃ molecules were photolyzed with the mercury arc and subsequently annealed, the resulting emission spectra were identical to those observed in the H₂S experiments.⁸ Further work also indicated that argon matrices containing OCS $+O_3$ or $H_2S + NO_2$ molecules produced the same chemiluminescence under the same conditions. Moreover, this chemiluminescence was observed only when both reactants were initially present. Since the only common uv-photolysis products of these reactants are sulfur atoms and oxygen atoms, we conclude that the emission carrier is an oxide of sulfur.

Concentration studies

Concentration studies indicated that the two new emission systems were greatly favored with respect to SO_2 phosphorescence at high matrix dilution. It was further noted in each experiment that the new systems were more prominent than SO₂ emission during the initial annealing of the matrix sample. During subsequent warmups, the new systems were reduced considerably in intensity with respect to that of SO₂. These observations suggest that the new emissions are caused by an excited intermediate in SO₂ formation, namely, SO*.

Oxygen isotopic data

Figure 2 illustrates the more intense emission system (labeled "C" in the earlier report) observed upon warmup of uv-photolyzed argon matrices containing H₂S and various ¹⁸O isotopically substituted ozone molecules. The top spectrum depicts the naturally abundant ozone case (H₂S + ${}^{16}O_3$), while the third trace is the spectrum observed upon warmup of a photolyzed matrix containing $H_2S + {}^{18}O_3$ molecules. The second spectrum was produced upon warmup of a photolyzed argon matrix containing H₂S and a partially ¹⁸O-enriched ozone sample and is simply a superposition of the two pure isotopic experiments. The doublet structure evident in





FIG. 2. Emission spectra in the 500-750 nm region recorded upon warmup $(8 \rightarrow 20 \text{ °K})$ of mercury-arc-photolyzed argon matrices containing (a) $H_2S + {}^{16}O_3$, (b) $H_2S + {}^{16}H_2O_3$, (d0% ${}^{18}O)$, (c) $H_2S + {}^{16}O_3$, and (d) OCS + ${}^{16}O_3$. Photolysis was performed for 2 h after total sample (~10 mmole) deposition.

the mixed-isotopic case confirms the presence of a *single* oxygen atom in the emitting species. The bottom trace of Fig. 2 represents the emission spectrum obtained upon warmup of a uv-photolyzed argon matrix sample containing OCS + ${}^{16}O_3$ molecules. The relative band intensities and frequency maxima are virtually identical to those observed in the H₂S + ${}^{16}O_3$ experiment (top trace). Table I summarizes the results of these oxygen isotopic experiments.

Several experiments were carried out in more dilute matrices in an effort to more precisely measure the

frequencies of the weaker "blue" emission system (labeled "B" in the earlier account). Figure 3 contains those emission spectra observed upon the initial warmup of two such dilute, uv-photolyzed matrices containing $H_2S + {}^{18}O_3$ and $H_2S + {}^{16}O_3$ molecules. The SO₂ phosphorescence spectrum, which is shown for comparison in the bottom trace of Fig. 3, was produced by a nearuv photolysis/warmup operation on an argon matrix sample containing OCS + O₂ molecules. Results from these experiments were also used in compiling Table I.

Temperature effects

As indicated previously, the observed SO_2 phosphorescence intensity, relative to the "B" and "C" emissions, grows markedly with time and increasing matrix temperature. This effect was used to advantage in locating the first several members of the weak "B" system. By recording the spectrum which appeared during the *initial*



FIG. 3. Emission spectra observed in the 350-550 nm spectral region following initial warmup $(8 \rightarrow 13 \rightarrow 8 \,^{\circ}\text{K})$ of dilute, mercury-arc-photolyzed matrices containing (a) $H_2\text{S} + {}^{18}\text{O}_3$, (b) $H_2\text{S} + {}^{16}\text{O}_3$, and (c) OCS + ${}^{16}\text{O}_2$. "B" and "C" emissions of SO are labeled accordingly. Small circles represent ${}^{18}\text{O}_2$ emissions. Unlabeled bands are $\text{SO}_2(a \rightarrow X)$ emissions.

TABLE I. Frequencies (cm⁻¹) and assignments of chemiluminescent emission bands observed during diffusion of argon matrices containing sulfur atoms and various combinations of isotopic oxygen atoms.

S + ¹⁶ O	S + ^{16,18} O	S + ¹⁸ O	Assignment ^a	$S + {}^{16}O$	S + ^{16,18} O	S + ¹⁸ O	Assignment ^a
25 906			в*3	20 342			C2
		25567	\mathbf{SO}_2^*			19982	B*9
25459			SO_2	19963	19964		SO_2
	25 4 28		\mathbf{SO}_2^*	19622	19631		В9
		25 046	$B*4, SO_2^*$			19390	C*3
24 974			B4, SO ₂	19243	19238		C3
	24 966		SO_2^*			19114	¹⁸ O ₂
		24 474	SO_2^*		19013	18 999	B*10
24 406			SO_2	18583	18 610(sh)		B10
	24 3 9 2		SO_2^*		18 497		?
		23 967	B*5, SO ₂ *		18315	18338	C*4
23 8 4 9	23825		В5, SO ₂	18160	18150		C4
		23423	SO_2^*			18020(sh)	B*11
23284			SO_2			17 908	¹⁸ O ₂
	23265		$S*O_2$	17553			B11
	22 950	22 9 9 4	B*6, ¹⁸ O ₂		17315	17352	C*5
22757	22733		B6, SO ₂	17120	17132		C5
		22 410	S*O ₂	16562			B12
	22282		$S*O_2$			16675	¹⁸ O ₂
22247			SO_2		16320	16325	C*6
	21 960	21 987	B*7, S*O ₂	16088	16 092		C6
		21767	¹⁸ O ₂		15353	15361	C*7
21 733	21706		B7	15072	15066		C7
		21 364	$S*O_2$		14362	14413	C*8
	21 264		S*O ₂	$14\ 063$	14070		C8
		20 99 5	B*8		13407	13411	C*9
21005			SO_2	13034	13075		С9
	20 982		S*O ₂			12469	C*10
20 675	20 638		B8	12079			C10
		20 472	C*2, ¹⁸ O ₂			11 549	C*11
	20 363		C2, C*2				

^aAsterisks indicate isotopically substituted species.

warmup (usually from 8 - 13 °K) and subtracting from it the spectrum which appeared in a later warmup (8 - 20 - 25 °K), it was possible to offset the interfering SO₂ phosphorescence spectrum. This procedure was applied to several oxygen isotopic experiments, and the resulting difference spectra are contained in Fig. 4.

It was further observed that each member of the "C" system was split into a poorly resolved doublet at warmup temperatures above ~ 30 °K. This doublet structure is illustrated in the lower trace of Fig. 5. Upon further warming to 35-40 °K, the weaker, higher-energy component gradually vanishes. The new high diffusion temperature band frequencies are listed in Table II.

Visible S₂ emissions

The visible emissions of S_2 in solid argon were observed in one blank experiment in which an Ar/H_2S = 300 matrix sample was subjected to mercury-arc radiation and subsequently annealed. In addition to the intense near-uv system of $S_2(B - X)$ which has been previously reported, ¹, ³, ⁵, ⁸ a weaker system of S_2 was observed in the visible region and a second intense S_2 system was located in the near-infrared region. These latter two systems have recently been reported by Pimentel *et al.* ^{12,13} Emission frequencies and spacings are contained in Table III.

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FIG. 4. Spectra in the 350-550 nm region resulting from the emissions observed in the first warmup attenuated by those of $SO_2(a \rightarrow X)$ observed in a later warmup. Experimental details given in text.

DISCUSSION

The reaction of ground state sulfur and oxygen atoms to form SO is exothermic by 124 kcal/mole¹⁴ and is therefore capable of populating electronic states less than 43 370 cm⁻¹ above the ground state. The two luminescence systems described above ("B" and "C") meet this requirement.

Red system

The assignment of the new intense red system ("C") to an electronic transition of molecular SO is strongly

TABLE II. Emission frequencies (cm^{-1}) of bands which appear at higher diffusion temperatures (>30° K) from argon matrices containing sulfur atoms and oxygen atoms.

ν _h	Δ	$\Delta(\nu_{\rm SO}-\nu_{\hbar})$
18100	•••	60
16 987	1013	133
15 968	1019	120
14 967	1001	105
13 984	983	79
		$\Delta v_{av_{\bullet}} = 100$

TABLE III. Frequencies (cm⁻¹) and spacings of chemiluminescent emissions following photolysis and warmup $(8 \rightarrow 20^{\circ} \text{K})$ of an Ar/H₂S = 300 matrix.

$S_2(\boldsymbol{B}^{3}\boldsymbol{\Sigma}_{\boldsymbol{u}}^{-} \rightarrow \boldsymbol{X}^{3}\boldsymbol{\Sigma}_{\boldsymbol{g}}^{-})^{\mathbf{a}}$		$S_2(A'^3\Delta_u -$	$S_2(A' {}^3\Delta_u \rightarrow X {}^3\Sigma_g)^b$		$S_2(c^{1}\Sigma_{u} \rightarrow a^{1}\Delta_{s})^{b}$	
Vobs	$\Delta \nu$	Vobs	$\Delta \nu$	Vobs	$\Delta \nu$	
27 141		17186	•••	14 984		
26440	701	16459	727	14289	695	
25758	682	15758	701	13590	699	
25108	650	15100(sh)	(658)	12 916	674	
24450	658			12264	652	
23 7 91	659	$\lambda_{1/2} \approx 238$	3 cm ⁻¹	11617	647	
23157	634	1/6				
22493	664			$\lambda_{1/2} \approx 20$	5 cm ⁻¹	
21865	633			172		
21232	628					
20614	618					
19970	644					
19334	636					
18684	650					
18 016	668					
$\lambda_{1/2} \approx 20$	09 cm ⁻¹					

^aAssigned according to Ref. 8.

^bAssigned according to Refs. 12 and 13.

supported by a detailed analysis of the oxygen isotopic data. Using standard least squares procedures, the most precise values of our data (Table IV) yield a T_0 of 22 543 cm⁻¹ for S¹⁶O and 22 570 cm⁻¹ for S¹⁸O. The value for the infrared fundamental calculated from ω_e and $\omega_e X_e$ for S¹⁶O is 1115.3 cm⁻¹, a value which is significantly lower than the reported vibrational frequency of SO in the gas phase (~1136 cm⁻¹)¹⁶⁻¹⁷ or in solid argon (1136.7 cm⁻¹).¹⁸ This would seem to sug-





TABLE IV. $SO[c^{1}\Sigma^{-}(v'=0) \rightarrow a^{1}\Delta(v''=2-11)]$ emission maxima (cm⁻¹) produced when argon matrices containing sulfur atoms and oxygen atoms are annealed. Spectroscopic constants were derived as described in text.

v''	S ¹⁶ O	S ¹⁸ O	$\Delta \nu$
2	(20 342) ^a	(20 472)	•••
3	19243	19390	147
4	18160	18338	178
5	17120	17352	232
6	16088	16325	237
7	15072	15361	289
8	14063	14413	350
9	13034	13411	377
10	12079	12469	390
11		11 549	•••
T_0	22 543 (cm ⁻¹)	22 570 (cm ⁻¹)	
ω	1130.7	1090.4	
ω.X.	-7.7	-7.4	
T _e	23 112 cm ⁻¹		
$\omega_{\theta}(\mathbf{S}^{18})$	$O)/\omega_{e}(S^{16}O) = 0.9644$	$\sqrt{\mu(S^{16}O/\mu(S^{18}O))}$)=0.9622

^aFrequencies in parentheses are estimates of overlapped bands and were not used in least squares calculations.

gest that the transition involved most likely terminates in an electronic state slightly above ground.

From a comparison with the known electronic states of S_2 and O_2 , ¹⁰ SO is expected to have three electronic states $(A''^{3}\Sigma^{+}, A'^{3}\Delta, \text{ and } c^{1}\Sigma^{-})$ approximately 28000 cm⁻¹ above the ground state in addition to the two known low-lying states at 10 500 cm⁻¹ $(b^{1}\Sigma^{+})^{17}$ and 6150 cm⁻¹ $(a^{1}\Delta)$.¹⁹ With this in mind, then, the most acceptable interpretation of the present data requires the assignment of the intense red SO system to a transition from one of the states near 28000 cm⁻¹ to the $a^{1}\Delta$ state at 6150 cm^{-1} . On the basis of the available data, the most reasonable assignment for this transition is $c^{1}\Sigma^{-} + a^{1}\Delta$, which is spin allowed but orbitally forbidden. Interestingly enough, the oxygen analog of this emission $(c^{1}\Sigma_{u} - a^{1}\Delta_{g})$ has recently been observed following ultraviolet excitation of O_2 (and its isotopes) in solid xenon²⁰ and ${}^{18}O_2$ in solid nitrogen. 21

Blue system

The "B" SO system is not as clearly defined as the red "C" system, since it is weaker and overlapped strongly by phosphorescent SO₂ emissions. The overlap problem was obviated somewhat by taking difference spectra as illustrated in Fig. 4. Although quite complex, the mixed oxygen isotopic experiment (middle trace, Fig. 4) appears to be merely a superposition of the two pure isotopic spectra shown in the top and bottom traces of Fig. 4. Again, as was the case for the red system, this is indicative of a species containing a single oxygen atom. The relative intensities of the "B" and "C" systems were approximately constant over a wide range of concentrations and at each of the several warmup temperatures below ~30 °K. On this basis, therefore, the blue "B" system is assigned to a second electronic transition of molecular SO.

A least squares analysis of the oxygen isotopic data, similar to that performed on the "C" system, yielded the ground state vibrational constants and electronic origin listed in Table V. The larger T_0 value of 28 400 cm⁻¹ (for S¹⁶O) suggests that this transition terminates in the ground electronic state of SO. This is further supported by the value calculated for the vibrational fundamental (1144.5 cm⁻¹, S¹⁶O), which is in satisfactory agreement with the directly observed argon matrix value of 1136.7 cm⁻¹.¹⁸

The most logical choices of assignment for this transition are $A''^{3}\Sigma^{+} \rightarrow X'^{3}\Sigma^{-}$ and $A''^{3}\Delta \rightarrow X'^{3}\Sigma^{-}$. Unfortunately, on the basis of the available evidence, we are not able to render a clear-cut decision. It is noted, however, that the traditional molecular oxygen $A^{3}\Sigma_{\mu}^{*} - X^{3}\Sigma_{\mu}^{*}$ emission system in solid argon has recently been reassigned as $C^{3}\Delta_{u} \rightarrow X^{3}\Sigma_{\kappa}^{-}$ on the basis of several vuv²⁰ and uv²¹ excitation studies of O2 molecules in inert cryogenic matrices. Moreover, this emission system of O_2 has been reported in an earlier publication⁸ from this laboratory as visible chemiluminescence generated from the O-atom recombination reaction in solid argon (although assigned at the time to $A \rightarrow X$ emission). In the case of S₂, the analogous $A'^{3}\Delta_{u} - X^{3}\Sigma_{s}^{-}$ system has recently been assigned^{12,13} to the visible emission observed in the 558-689 nm region observed upon warmup of argon matrices containing ground state sulfur atoms. Consequently, by analogy with the O_2 and S_2 cases, we tentatively assign the blue "B" emission system of SO to the $A'^{3}\Delta - X^{3}\Sigma^{-}$ electronic transition.

O-atom reactions

The only chemiluminescence observed following 632.8 nm photolysis and warmup of dilute argon matrices containing $H_2S + O_3$ molecules was that attributable to SO_2 phosphorescence $(a \rightarrow X)$. This result lends further support to the reaction mechanism proposed by Smardzewski and Lin, ⁶ who observed the infrared spectrum of HSOH following similar reactions. Their mechanism is as follows:

$$\mathcal{D}(^{3}P) + \mathcal{H}_{2}S \rightarrow [\mathcal{H}_{2}S = \mathbf{O}]^{\dagger}, \qquad (1)$$

$$[H_2S = O]^{\dagger} - [HSO + H]_{cage} - HSOH, \qquad (2)$$

$$\left[\mathrm{H}_{2}\mathrm{S}=\mathrm{O}\right]^{\dagger} \rightarrow \mathrm{H}_{2} + \mathrm{SO}, \tag{3a}$$

$$\rightarrow$$
 HSO + H . (3b)

Since this pathway to SO formation is exothermic by ~53 kcal/mole (~18500 cm⁻¹/molecule), it is not surprising that the SO emissions ("B" and "C") were not observed in this system. It is possible, however, to form excited SO₂ by the secondary reactions of oxygen atoms with SO (or HSO)⁶ from Reaction (3):

$$O(^{3}P) + SO(HSO) \rightarrow SO_{2}^{*} , \qquad (4)$$

which ultimately leads to SO₂ phosphorescence.

Similar experiments were attempted after 632.8 nm photolysis of argon matrices containing OCS + O_3 molecules. In this case, however, virtually no luminescence

TABLE V. $SO[A'^{3}\Delta(v'=0) \rightarrow X^{3}\Sigma^{-}(v''=4-11)]$ emission maxima (cm⁻¹) observed when argon matrices containing sulfur atoms and oxygen atoms are annealed. Ground state numbering was estimated from the difference between unblended S¹⁶O and S¹⁸O bands.

$v^{\prime\prime}$	S ¹⁶ O	S ¹⁸ O	$\Delta \nu$
4	(23 849) ^a	(23 967)	••••
5	(22757)	(22 994)	•••
6	21733	21 987	254
7	20675	20 995	320
8	19622	19982	360
9	18583	18 992	409
10	17 553	(18020)	
11	16551		
T_0	28400 (cm ⁻¹)	b	
ώe	1157.9		
$\omega_{e}X_{e}$	-6.7		

^aFrequencies in parentheses are estimates of overlapped bands and were not used in least squares calculations.

^bLeast squares fit was not done for S¹⁸O since only a limited data set was available. Vibrational assignments were determined by extrapolating $\Delta \nu$ and are only accurate to ±1 unit.

was observed during matrix warmup. This result suggests that the reaction

$$O(^{3}P) + OCS - CO_{2} + S , \qquad (5)$$

although exothermic by ~53 kcal/mole, apparently does not occur under the present conditions, since either SO or SO₂ chemiluminescence should have followed (from the S + O reactions). Presumably, this is due to a nonzero activation energy for Reaction (5). The alternative abstraction reaction forming CO and SO is also exothermic but has a known activation energy of ~5 kcal/ mole, ^{22, 23} which would preclude its occurrence at these cryogenic temperatures (~20 °K).

Temperature effects

Figure 5 shows the structure which appears in the more intense SO emission system ("C") at the higher warmup temperatures. Since the spacings are approximately the same, we ascribe this behavior to matrix effects, perhaps due to reactions occurring at the gassolid interface as the matrix begins to sublime. It seems more plausible, however, that the splitting is caused by the resolution of the zero phonon lines (ZPL) from the phonon wing. When oxygen atoms recombine at $\sim 20^{\circ}$ K in solid argon, the observed emissions⁸ are red shifted an average of $\sim 80 \text{ cm}^{-1}$ from the ZPL's observed during photoexcitation of O_2 in solid argon.²¹ Presumably, the red shift is due to unresolved phonon structure in the chemiluminescence experiments. For the analogous case of our SO results, the average difference between our proposed ZPL's (the higher energy components of the high temperature doublets) and the frequencies observed during initial warmup is ~100 cm⁻¹ (Table II), a value which is consistent with this interpretation.

S₂ chemiluminescence

In the blank Ar/H₂S experiments, the observed S₂ chemiluminescent systems peaking near 600 and 750 nm were identical to those reported recently by Pimentel *et al.*, ^{12,13} who assigned them to the $A'{}^{3}\Delta_{u} \rightarrow X {}^{3}\Sigma_{g}^{-}$ and $c^{1}\Sigma_{u}^{-} + a^{1}\Delta_{g}$ transitions of molecular S₂, respectively. These are apparently the S₂ analogs of the SO emissions ("B" and "C") which are assigned to similar electronic transitions (viz., $A'{}^{3}\Delta \rightarrow X {}^{3}\Sigma^{-}$ and $c^{1}\Sigma^{-} + a^{1}\Delta_{0}$.

CONCLUSIONS

When ground state sulfur atoms and oxygen atoms combine in solid argon at 8-40°K, several chemiluminescent systems due to SO and SO_2 are present. The red (490-870 nm) and blue (385-600 nm) SO emissions have been identified and characterized as $c^{1}\Sigma^{-} + a^{1}\Delta$ and $A'^{3}\Delta - X^{3}\Sigma^{-}$ transitions, respectively, from the spectroscopic parameters determined from the oxygen isotopic data. The argon matrix reaction of ground state oxygen atoms $O(^{3}P)$ with H₂S molecules was shown to produce only SO₂ phosphorescence (a - X), which is consistent with the formation of an excited formaldehyde-type intermediate H₂SO. The analogous matrix reactions of O atoms and OCS molecules generated no chemiluminescence, which suggests that the reaction of atomic oxygen with OCS to produce S atoms and CO_2 has a nonzero activation energy.

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