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Chemiluminescent matrix reactions of atomic oxygen, sulfur, and $O(^3P)+H_2S$

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Optical multichannel techniques have been used to analyzed the visible chemiluminescence generated by diffusion-controlled warmup (8→20°K) of separate, uv-photolyzed inert gas matrices containing O_3, H_2S, H_2S+O_2, and O_3+H_2S molecules. Oxygen atoms were observed to diffuse and recombine in solid argon at ~17°K to produce the intense Herzberg I band system of molecular O_2 ($A \rightarrow X$) which was also observed in krypton though not in xenon matrices. The lack of any detectable emission in xenon was attributed to premature diffusion and depletion of atomic oxygen prior to diffusion-controlled warmup. Matrix diffusion and recombination of sulfur atoms produced intense S_2 emission ($B \rightarrow X$) in all three matrices (Ar, Kr, Xe). Long, structured vibrational progressions ($0,v''$) were observed in argon and krypton, while a broad, relatively structureless emission was observed in xenon. Suggested mechanisms for this latter effect include such processes as vibrationally unrelaxed fluorescence and/or S_2^*–Xe van der Waals "complex" formation. Diffusion of sulfur atoms in matrices containing traces of molecular O_2 produced the phosphorescent emissions of SO_2 ($a \rightarrow X$) which appeared to be orders of magnitude more intense than the S_2 emissions. Oxygen atoms were observed to diffuse and react with H_2S molecules in dilute argon matrices at ~14°K, thereby generating SO_2 phosphorescence ($a \rightarrow X$) as well as two emission systems of lesser intensity (520–675 nm), each with an approximate vibrational spacing of ~1040 cm^{-1}. Suggested emitter(s) responsible for these latter chemiluminescent systems are presented.

INTRODUCTION

In the course of some recent investigations[1,2] in this laboratory concerning the matrix reactions of oxygen atoms with H_2S molecules an intense blue–violet chemiluminescence was observed when mercury-arc photolyzed argon matrix samples, initially containing O_3 and H_2S molecules, were warmed from 8 to ~20 °K. This emission was subsequently identified from spectral photographs as SO_2 phosphorescence ($a\,^3B_1 \rightarrow X\,^1A_1$). A similar emission system ($a \rightarrow X$) was also photographically identified by Lalo *et al.*[3] in their earlier study of the luminescence produced by warmup of VUV-photolyzed matrices containing SO_2. Brom and Lepak[4] had reported this same emission system as a "blue afterglow" following VUV photolysis of OCS in argon matrices, although they incorrectly ascribed it to excited OCS formed by the cage recombination reaction $S+CO \rightarrow OCS^*$. This was pointed out by Long and Pimentel[5] in their $O_2(^{18}O_2)$-doped studies where they attribute the SO_2 phosphorescence as arising from the $S+O_2$ matrix diffusion reaction.

Another source of luminescence in several of these systems involves the radiative recombination of ground state sulfur atoms to produce electronically excited S_2. One of the earliest reports of this was the work of Barnes *et al.*[6] These workers, who observed a "blue–purple glow" on warming (30 °K) several mercury-arc photolyzed matrices containing H_2S molecules, attributed it to S_2 fluorescence produced as a consequence of the $S+S \rightarrow S_2^*$ diffusion reaction. Confirmatory evidence for this process was provided in the OCS photolysis experiments of Brom and Lepak[4] and more recently by Fournier *et al.*[7] in their CS_2 photolysis studies. These latter workers also recorded the intensity variation as a function of temperature (glow curves).

In each of these previous accounts of chemiluminescent matrix processes the light emitted by the various samples was detected, after spectral dispersion, by either a conventional, single-element photomultiplier tube or a photographic plate. The chief disadvantage of using a single-channel PM tube in these experiments lies in the fact that the photon flux, which is proportional to the concentration of the emitting species (viz. SO_2^*, S_2^*) in the matrix, is changing during the time required for scanning a spectrum. Consequently, relative band intensities within a particular emission system can only be approximated. This difficulty is obviated by the use of a photographic plate when all wavelengths are detected simultaneously after dispersion. However, the inherently low gain and logarithmic response of even a high speed photographic emulsion limits its application to only those more intense chemiluminescent systems. A logical alternative to both of these devices is the TV-type silicon vidicon tube or optical multichannel analyzer (OMA).[8–11] In such a system the multichannel capabilities of a photographic plate are coupled with the high gain and linear response characteristics of a photomultiplier tube. With this in mind then the techniques of optical multichannel spectroscopy were applied to an examination of chemiluminescent matrix reactions in general and the O_3–H_2S system in particular. Herein follows a detailed matrix isolation study of the chemiluminescent matrix reactions of atomic oxygen, sulfur, and $O(^3P)+H_2S$ as provided by the controlled warmup, after photolysis, of various matrices containing O_3, H_2S, H_2S+O_2, and O_3+H_2S molecules.

EXPERIMENTAL

Gaseous hydrogen sulfide (Matheson Gas products, 99.5% minimum purity) was used without further purification in a thoroughly passivated vacuum manifold fabricated from 316 stainless steel with Teflon as the gasket material. The ozone samples were prepared by a high voltage discharge of oxygen gas (Matheson Gas Products, 99.6% minimum purity), followed by subse-

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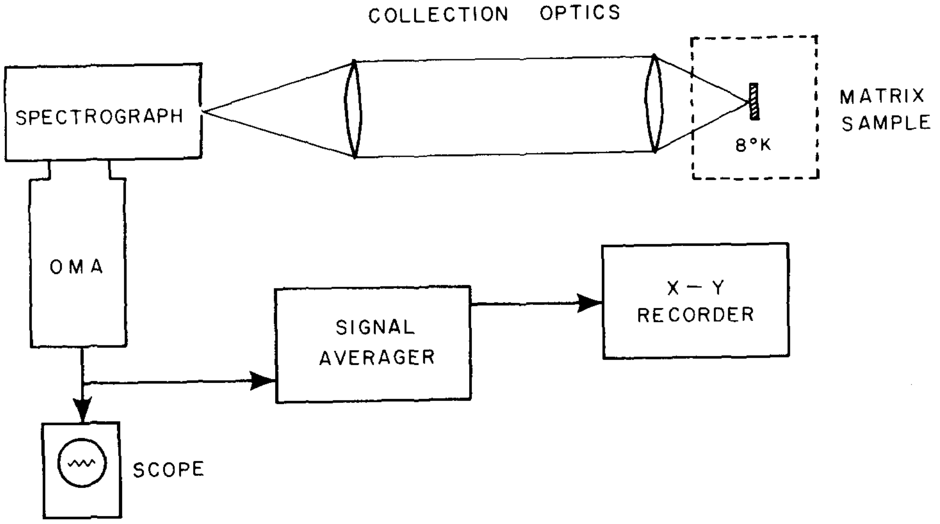

FIG. 1. Schematic diagram of the chemiluminescence apparatus.

quent condensation at liquid nitrogen temperatures. Oxygen-18-enriched ozone was similarly prepared from $^{18}O_2$ (Miles Laboratories, Inc., 99.4% ^{18}O). Argon (Linde prepurified, 99.998%), which was employed as the primary matrix material in most experiments, was used without further treatment as were the krypton (Linde research grade, 99.995%) and xenon (Matheson research grade, 99.995%) gas diluents.

The overall arrangement of the vacuum vessel, cryogenic refrigeration system, and gas manifold have been described elsewhere.[12] Two important modifications for the present study were the replacement of the CsI cold window with a highly polished, steeply pitched copper wedge, and the use of Suprasil optical plates (2 in. diam., 1/8 in. thick, Esco Products, Inc., grade S1) for the outer shroud windows. The ozone and/or hydrogen sulfide samples, diluted in the appropriate inert gas, were deposited from separate, passivated stainless steel manifolds onto the copper wedge which was maintained at a temperature near 8 °K. Prior to the start of every experiment, an argon underlayment (1m*M*) was deposited in order to minimize any possible corrosion of the copper support. Deposition rates through each spray-on line were monitored and maintained at 1.1–2.9m*M*/h for 2–6 h by previously calibrated thermocouple gage readings downstream of the vernier metering valves (Hoke-1315G4Y).

The majority of the photolysis experiments were performed with a low pressure mercury arc lamp (GE H85A3/UV) with the glass envelope removed. Photolytic radiation was focused onto the various samples, either during or after the deposition procedure, through a biconvex quartz lens (2 in. diam., 3 in. focal length) accompanied by a 5 cm water filter. In several experiments a high pressure quartz–mercury vapor lamp (Philips HPK 125W) was used as the source of photolytic radiation. No observable increase in matrix temperature was noted during the periods of irradiation.

After complete sample deposition and photolysis the temperature of the matrix was slowly increased. This was accomplished, in the initial experiments, by precise control of the current applied to a wire-wound resistance heater in contact with the copper wedge. In later experiments, however, it was observed that simple shutdown of the closed-cycle helium refrigerator (Air Products Displex model CSW-202) was sufficient to afford slow sample warmup (1–3 °K/min) due to the ballasting capacity of the copper wedge as a heat sink. Matrix temperatures in the 8–40 °K region were monitored by a chromel vs. Au-0.07 at% Fe thermocouple used in conjunction with a fast-responding digital millivoltmeter (Keithley Model 160B). A hydrogen vapor pressure gage was also employed as a secondary indicator of sample temperature.

Emission spectra were recorded at various warmup temperatures with a modified Jarrel-Ash model 1208 0.3 m monochrometer which incorporated a low dispersion grating (147.5 grooves/mm) blazed at 500 nm. The optical layout, which is illustrated in Fig. 1, consisted simply of a collection lens (quartz, 2 in. diam., 3 in. focal length) which collimated the light emitted from a *small point area* of the matrix sample onto a focusing lens (2 in. diam., 10 in. focal length) which was situated in front of the entrance slit (25 μ) of the monochrometer. Emitted light was collected from a *small point area* of the matrix sample in an effort to minimize the inhomogeneous heating effects that occurred as a consequence of the varying thickness of the deposit (i.e., some spots on the surface of the matrix were heated faster/slower than others). The spectrally dispersed light was detected by a silicon intensified target (SIT) vidicon tube fitted with a uv scin-

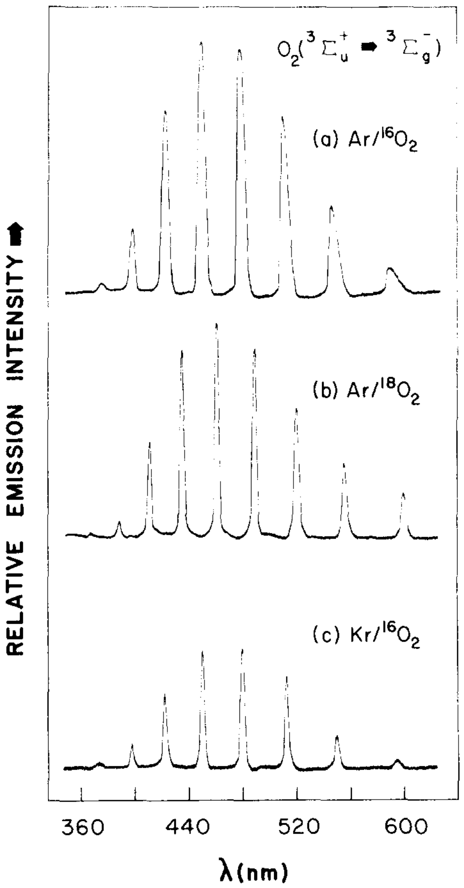

FIG. 2. Emission spectra recorded upon warmup (8 → 17 °K) of argon and krypton matrices containing O_3 molecules which had been deposited at 8 °K and subsequently subjected to mercury-arc photolysis (15 min). (a) Ar/$^{16}O_3$ = 100; 97μ*M* $^{16}O_3$; (b) Ar/$^{18}O_3$ = 100; 140μ*M* $^{18}O_3$; (c) Kr/$^{16}O_3$ = 100; 87μ*M* $^{16}O_3$.

tillator (Princeton Applied Research, model 1205D/01). In a few experiments an image intensified vidicon tube (ISIT) was used as a detector (Princeton Applied Research, model 1205I/01), the chief difference between the two being the enhanced red response in the case of the ISIT tube. Overall spectral response varied between 10^{-2}–10^{-1} counts/photon across the 200–650 nm wavelength region. Individual digitized spectra, stored in 500 channels which traversed a particular 275 Δ(nm) spectral region, were read out at the rate of 32.8 mS/scan and stored in an accumulator (Princeton Applied Research model 1205A) for processing (e.g., signal averaging, background subtraction). In every experiment described in this investigation 1000 individual scans were accumulated and signal averaged in a 32.8 sec time interval, during which period the temperature of the matrix sample remained constant to within +1–2 °K. Final accumulated spectra were displayed on a storage oscilloscope (Tektronix model 605) and plotted on an *X*–*Y* recorder (Hewlett-Packard model 7044A) after suitable *D* → *A* conversion. A mercury pen lamp (Spectroline) was utilized as a source of calibration lines, and the 365.0, 404.7, 435.8, 507.3 (2 × 253.7), 546.1, 577.0, and 579.1 nm emission lines of the mercury discharge were employed as on-line standards. The spectral resolution element was 0.55 nm/channel while the absolute wavelength accuracy was estimated at ± 1 nm.

RESULTS

O_3 photolysis

When a dilute O_3 argon matrix sample (Ar/O_3 = 100) was condensed onto the 8 °K copper substrate, subjected to ~ 15 min of photolysis, and subsequently warmed to ~ 17 °K the emission spectrum displayed in Fig. 2 was obtained. The emission was reversibly quenched as the matrix was recooled to 8 °K. In this manner several warmup cycles could be performed on the same matrix sample. Increased luminescent intensity, however, was observed only if the temperature in a particular warmup cycle was greater than that in any preceding cycle. The intense vibrational progression in the 360–660 nm spectral region exhibited an average spacing of 1369 cm^{-1} with appreciable anharmonicity. Observed frequency maxima are contained in Table I. Absolute matrix frequencies were observed to remain constant over the range of temperatures studied (15–22 °K). Upon ^{18}O-isotopic substitution the band maxima shifted to higher energies with a smaller average spacing (1313 cm^{-1}). The average bandwidths were also observed to decrease in the ^{18}O experiments [i.e., $\overline{\Delta\nu_{1/2}}$ = 314 cm^{-1}(^{16}O), 160 cm^{-1}(^{18}O)]. From the observed frequencies and relative intensities of these spectral features it became clear that this emission was the forbidden $A\,^3\Sigma_u^+ - X\,^3\Sigma_g^-$ Herzberg I system of molecular oxygen.[13,14] A comparison of the frequencies of the (0, ν'' = 5–12) bands of gas phase O_2[13] with the present argon matrix values revealed an average gas → matrix shift of 940 ± 20 cm^{-1} (av. deviation) to lower wavelengths.

The analogous warmup experiments in krypton matrices yielded the same long progression series with similar spacings (average = 1374 cm^{-1}) and an average Ar → Kr matrix shift of − 46 cm^{-1} for the absolute frequencies. In contrast to the argon case, however, it was noted that the overall intensities were considerably reduced in the krypton experiments, so much so that, in several cases, depending upon the desired temperature, only one warmup was possible.

TABLE I. $O_2(A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-)$ emission band maxima (cm^{-1}) produced as a result of warmup (8 → 17 °K) of photolyzed argon and krypton matrices containing O_3 molecules (*M*/*R* = 100).

Ar/$^{16}O_2$[a]		Ar/$^{18}O_2$		Kr/$^{16}O_2$		(0, ν'')[b]
26 539		27 137		26 511		(0, 5)
25 038	1501	25 674	1463	25 025	1486	(0, 6)
23 657	1381	24 290	1384	23 596	1429	(0, 7)
22 267	1390	22 989	1301	22 212	1384	(0, 8)
20 881	1386	21 678	1311	20 829	1383	(0, 9)
19 569	1312	20 400	1278	19 501	1328	(0, 10)
18 245	1324	19 139	1261	18 198	1303	(0, 11)
16 938	1307	17 902	1237	16 892	1306	(0, 12)
15 588	1350	16 633	1269			(0, 13)
		15 319	1314			(0, 14)

[a] Average of seven experiments.
[b] Assigned according to Ref. 22.

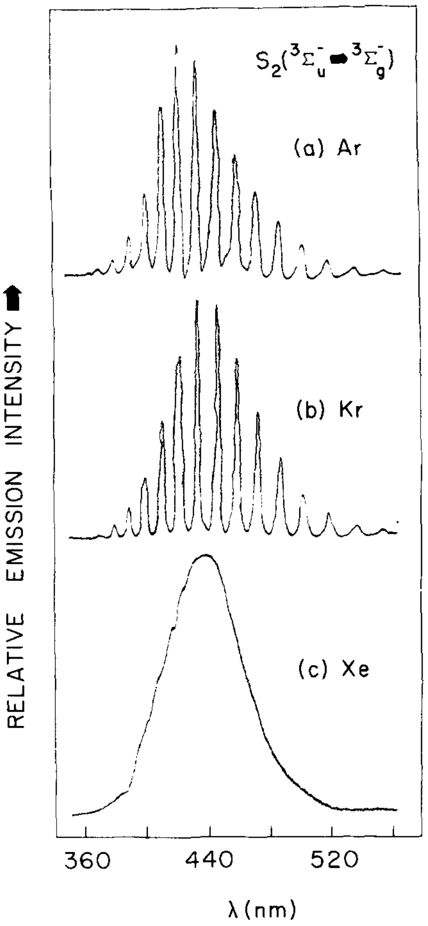

FIG. 3. Chemiluminescent emissions observed upon warmup (8 → 13–15 °K) of H_2S-containing matrices ($M/H_2S = 100$, M = Ar, Kr, Xe) which had been irradiated (mercury-arc) during deposition at 8 °K. (a) 19*μM* H_2S; (b) 83*μM* H_2S; (c) 86*μM* H_2S, 15 °K.

Several O_3-photolysis-warmup experiments were conducted in xenon matrices. In each case, however, no observable emission was recorded even under conditions of maximum spectral accumulation (full dynamic range). Apparently, the intensity of the emission was reduced to such an extent that it was below the detection capabilities of our system (SIT–OMA).

H_2S photolysis

Argon matrices containing H_2S molecules ($Ar/H_2S = 100$) were photolyzed during the deposition procedure and subsequently warmed to 13–25 °K. The intensity of the emission generated in this fashion was observed to be appreciably greater than that produced in similar experiments where photolysis was performed after complete sample deposition. The resultant chemiluminescence spectrum, as illustrated in Fig. 3, consisted of a long series of sharp bands in the 365–560 nm region. Absolute emission frequencies are contained in Table II. This banded spectrum was identified as $S_2(B\,^3\Sigma_u^- \rightarrow X\,^3\Sigma_g^-)$ emission on the basis of coincidence of the measured wavelengths and intensities with the uv-excited fluorescence spectrum of S_2 in an argon matrix.[15] Analogous experiments using krypton as the matrix material produced a similar, though slightly sharper [$\overline{\Delta\nu}_{1/2}$(av.) = 243 cm^{-1}(Ar), 205 cm^{-1}(Kr)], emission spectrum with similar vibrational spacings [average = 653 cm^{-1}(Ar), 650 cm^{-1}(Kr)]. The absolute frequencies were observed to shift to lower energies in krypton [$\overline{\Delta\nu}(Ar \rightarrow Kr) = -613$ cm^{-1}]. In xenon matrices a rather unexpected result was obtained. The structured luminescence in the argon and krypton experiments was observed only as a broad emission (365–532 nm) in solid xenon, with little, if any, resolvable structure (Fig. 3).

At warmup temperatures greater than ~26 °K additional spectral features began to grow in intensity in all three matrices. Eventually, after several minutes those emission features of S_2 were apparently overwhelmed and replaced by a different luminescing system which was subsequently identified as $SO_2(a\,^3B_1 \rightarrow X\,^1A_1)$ phosphorescence.[16,17] A possible explanation for this finding is that traces of molecular oxygen impurity may diffuse at significantly enhanced rates at these higher matrix temperatures and subsequently react with sulfur atoms generated via H_2S photolysis. Other workers[5] had reached a similar conclusion in related OCS-photolysis experiments with O_2 impurity levels of the order of ~0.1%. Nevertheless, in order to verify this in the present investigation identical photolysis studies were carried out on oxygen (O_2)-doped H_2S matrix samples.

$H_2S + O_2$ photolysis

When argon, krypton, and xenon matrix samples containing H_2S and ~1% O_2 (i.e., $Ar, Kr, Xe/H_2S/O_2 = 100/1/1$) were subjected to photolysis during deposition, followed by warmup to ~17 °K, the emission spectra represented in Fig. 4 were obtained. Frequencies and vibrational spacings are contained in Table III. In all three matrices the luminescence was identified as being predominantly due to SO_2 phosphorescence ($a \rightarrow X$)

TABLE II. $S_2(B\,^3\Sigma_u^- \rightarrow X\,^3\Sigma_g^-)$ emission band maxima (cm^{-1}) produced as a result of warmup (8 → 13 °K) of photolyzed matrices containing H_2S molecules: $(Ar, Kr, Xe)/H_2S = 100$.

Ar		Kr		Xe[a]	$(0, \nu'')$[b]
		27 263		27 400 (< 1% I_{max})	(0, 5)
27 196		27 539	724	|	(0, 6)
26 483	713	25 860	679	↓	(0, 7)
25 793	690	25 157	703	broad, unresolved	(0, 8)
25 107	686	24 486	671	emission	(0, 9)
24 456	651	23 821	665	|	(0, 10)
23 781	675	23 164	657	↓	(0, 11)
23 137	644	22 517	647	22 880 (I_{max})	(0, 12)
22 492	645	21 858	659	|	(0, 13)
21 853	639	21 222	636	|	(0, 14)
21 213	640	20 585	637	|	(0, 15)
20 576	637	19 948	637	|	(0, 16)
19 928	648	19 324	624	↓	(0, 17)
19 298	630	18 723	601	18 800 (< 1% I_{max})	(0, 18)
18 632	666	18 106	617		(0, 19)
18 060	572	17 507	599		(0, 20)

[a] 15 °K.

[b] Assigned according to Ref. 15.

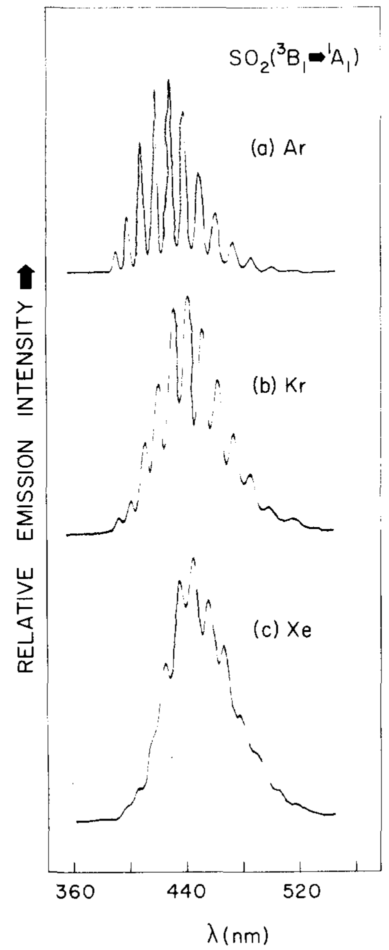

FIG. 4. Emission spectra observed upon warmup (8 → 18 °K) of argon, krypton, and xenon matrices containing H_2S+O_2 molecules ($M/H_2S/O_2=100/1/1$) which had been subjected to mercury-arc irradiation during sample deposition at 8 °K. (a) 35μM H_2S; (b) 72μM H_2S; (c) 137μM H_2S.

comprising the intense vibrational progression $a(0,0,0) \rightarrow X(v_1'', v_2'', 0)$. Specific bands were assigned on a comparative basis with the earlier SO_2 matrix phosphorescence results (uv-excited) of Meyer and co-workers.[16,17] Emission maxima were displaced to lower energies on going from argon to xenon matrices and average frequency shifts were estimated at Ar(0), Kr($-116\,\text{cm}^{-1}$), and Xe($-296\,\text{cm}^{-1}$). Bands were observed to broaden on going from argon to xenon. In fact, this occurred to such an extent in the case of xenon that a number of emission maxima had to be estimated.

In every case involving H_2S+O_2 photolysis those emissions attributable to S_2 fluorescence ($B \rightarrow X$) were observed only very weakly if at all. Apparently, the SO_2 phosphorescence is orders of magnitude stronger than any S_2 fluorescence. Caution was taken, however, before arriving at such a conclusion, since a careful comparison of the S_2 emission spectrum (argon matrix) with that of SO_2 revealed extensive overlap (Fig. 5). The two emission systems can be distinguished by their spectral differences above 450 nm and below ~415 nm. Unfortunately, however, both emission systems exhibit their weaker features outside this 415–450 nm wavelength interval. Moreover, it was observed in the H_2S+O_2 argon matrix studies that, at temperatures above ~25 °K, the SO_2 phosphorescence maxima were displaced to lower energies. For example, as the warmup temperature was increased from 17 to 34 °K, the emission maxima were red shifted an average of $-166 \pm 19\,\text{cm}^{-1}$. Thus, it became rapidly obvious that extreme care must be taken when distinguishing between various chemiluminescent systems in matrices.

TABLE III. $SO_2(a\,^3B_1 \rightarrow X\,^1A_1)$ phosphorescence band maxima (cm^{-1}) produced as a result of warmup (8 → 18 °K) of photolyzed matrices containing H_2S and O_2 molecules: (Ar, Kr, Xe)/$H_2S/O_2=100/1/1$.

Ar		Kr		Xe		Assignment[a]
25 465		25 272		25 145[b]		000
24 938	527	24 771	501	24 582[b]	563	010
24 331	607	24 166	605	23 958[b]	624	100
23 793	538	23 669	497	23 447	511	110
23 229	564	23 105	564	22 894	553	120
22 686	543	22 553	552	22 401	493	130
22 148	538	21 993	560	21 853	548	220
21 584	564	21 492	501	21 340	513	230
21 061	523	20 960	532	20 803[b]	537	320
20 504	557	20 442	518	20 284[b]	519	···
19 928	576	19 920	522	19 662[b]	622	···
19 361	567	19 294	626	19 106[b]	566	···
		18 598	696			

[a] Assigned according to Ref. 17. [b] Estimated.

$O_3 + H_2S$ photolysis

The chemiluminescent matrix reactions of ground state atomic oxygen $O(^3P)$ with H_2S were investigated

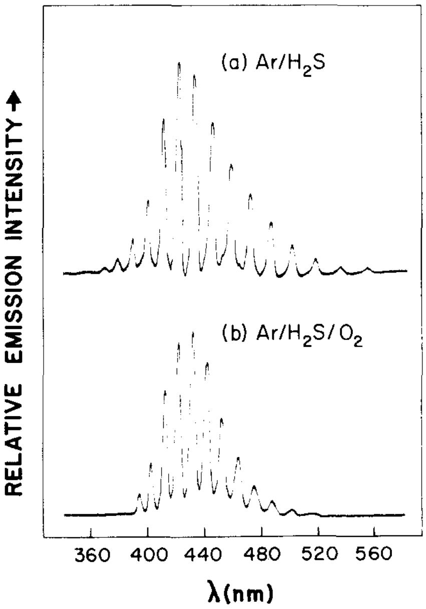

FIG. 5. Comparison of emission spectra recorded upon warmup of separate argon matrices containing H_2S and H_2S+O_2 molecules which had been exposed to near uv radiation during deposition at 8 °K. (a) $Ar/H_2S=100$, 19μM H_2S, 13 °K; (b) $Ar/H_2S/O_2=100/1/1$, 35μM H_2S, 18 °K.

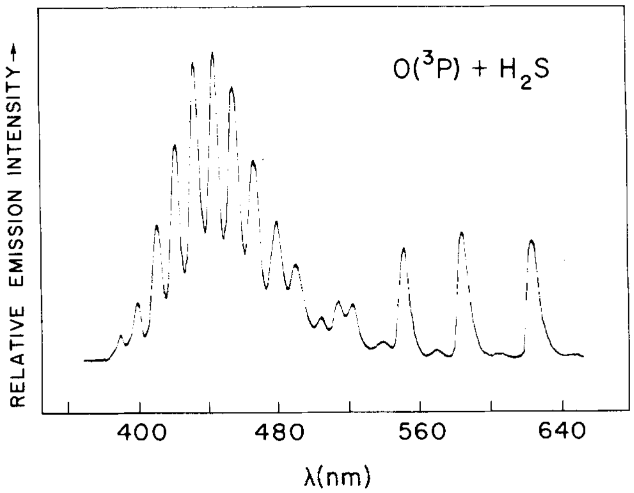

FIG. 6. Chemiluminescent emissions observed upon warmup (8 → 14 °K) of a matrix sample codeposited at 8 °K from separate $Ar/O_3 = 100$ and $Ar/H_2S = 100$ mixtures, followed by 15 min of mercury-arc photolysis. $Ar/O_3/H_2S = 238/1.4/1.0$; 92$\mu M$ H_2S.

via *in situ* matrix photolysis of argon matrices containing O_3 and H_2S molecules. In these experiments a dilute O_3 argon matrix sample ($Ar/O_3 = 100$) was simultaneously condensed with a similar H_2S sample ($Ar/H_2S = 100$) onto the 8 °K copper support. After a short period of ultraviolet photolysis (~15 min) the matrix sample was warmed to a specific temperature and the emission spectrum recorded (Fig. 6). In most cases the intense banded luminescence appeared almost immediately upon warming, with three distinct emission systems being evident (Fig. 6). Frequency maxima and vibrational spacings are contained in Table IV. A number of warmup experiments were conducted between temperatures of 11–24 °K, with no apparent frequency shifts being observed.

The most intense emission system was that detected in the 390–520 nm spectral region (labeled A in Table IV). The frequency positions, relative intensities, and vibrational spacings were very similar, though not identical, to those values observed in the $H_2S + O_2$ experiments and attributed to SO_2 emission ($^3B_1 - {}^1A_1$). Consequently, we also assign this particular luminescence to SO_2 phosphorescence. In the $O_3 + H_2S$ case, however, the phosphorescence maxima were displaced to slightly higher energies ($+72 \pm 26\ cm^{-1}$).

A less intense emission system (labeled C in Table IV) was detected in the 520–675 nm region which consisted of a progression of five bands with an average spacing of ~1076 cm^{-1} and an average linewidth of 230 cm^{-1}. A third, much weaker, luminescent system (B) was also observed in the same general wavelength region. In this case, however, only a few members of the progression were observed (average spacing = 999 cm^{-1}). The exact nature of the emitter(s) responsible for these last two chemiluminescent systems is not presently known. Any emissions of $O_2(A\,^3\Sigma_u^+ \to X\,^3\Sigma_g^-)$ or $S_2(B\,^3\Sigma_u^- \to X\,^3\Sigma_g^-)$ were either not present or too weak for observation.

DISCUSSION

Oxygen atoms

The dominant contributor to the ultraviolet spectrum of the night afterglow is the forbidden $A\,^3\Sigma_u^+ \to X\,^3\Sigma_g^-$ Herzberg I system of molecular oxygen.[18,19] Broida and Peyron,[20] in a series of elegant emission studies of solids at low temperatures, had observed this same system (340–640 nm) upon condensing the products of nitrogen discharges containing traces of oxygen. However, their assignment of the upper state to $A\,^3\Sigma_u^+$ has recently been questioned.[21] Energy transfer from excited N_2 was postulated as a mechanism of excitation, although atom diffusion in the solid was pointed out as a distinct possibility. Electron bombardment[22] of O_2-containing rare gas solids was also observed to generate a similar series of emission lines.

The results of the present investigation (Table I, Fig. 2) are in close agreement with the frequencies and intensities reported in these earlier discharge[20] and electron bombardment[22] studies. Frequencies differ, on the average (including sign), by −96 and −77 cm^{-1} with spacings differing by ~15 and 13 cm^{-1} for the Ar/O_2 and Kr/O_2 cases, respectively. In the present experiments, however, the most probable mechanism of excitation, which can account for this luminescence, is the radiative recombination of O atoms which diffuse and recombine at the higher matrix temperatures where the inert gas solid loses its rigidity. Moreover, after several hours or even minutes in a cryogenic solid at 8 °K any oxygen atoms which may be initially produced in an excited state configuration [i.e., O(^1D)] are completely quenched to their ground electronic state [O(^3P)].

TABLE IV. Chemiluminescent emissions (cm^{-1}) observed after warmup (8 → 14 °K) of a photolyzed argon matrix containing O_3 and H_2S molecules: $Ar/O_3/H_2S = 238/1.4/1.0$; 92$\mu M$ H_2S.

Emission (cm^{-1})		Δ(cm^{-1})		Assignment
25 342				
24 877	465			
24 278	599			
23 730	548			
23 202	528			
22 640	562			*A*
22 060	580			
21 501	559			
20 921	580			
20 458	463			*A* + *B*
19 865	593			*A*
19 497		961		*B*
19 168				*C*
18 529		968		*B*
18 116			1052	*C*
17 516		1013		*B*
17 044			1072	*C*
16 461		1055		*B*
15 954			1090	*C*
14 863			1091	*C*

We therefore conclude that it is the matrix diffusion and recombination of $O(^3P)$ atoms that is responsible for the intense banded chemiluminescence, identified as the Herzberg I system of molecular O_2, which is produced upon warmup of photolyzed matrices containing traces of O_3:

$$O(^3P)+O(^3P)+M\rightarrow O_2(A\,^3\Sigma_u^+\rightarrow X\,^3\Sigma_g^-)+M\,. \qquad (1)$$

The $A\,^3\Sigma_u^+$ state is known[23] to be produced mainly by recombination of oxygen atoms in argon discharges. Apparently, a similar process occurs in solid argon and krypton with the chief difference being that the upper state $(A\,^3\Sigma_u^+)$ is vibrationally quenched in these solids.

The diminished emission intensities in krypton and the total absence of any detectable luminescence in xenon can be accounted for by the enhanced diffusion of oxygen atoms *during* the photolysis period. A smaller oxygen atom may diffuse[24] to such an extent in solid krypton or xenon at 8 °K that the great majority of them are effectively scavenged (to produce O_2 and O_3) before commencement of the warmup cycles. Although radiative quenching by krypton or xenon does play a role in this intensity variation with matrix material, we consider it minor in view of the fact that the Herzberg I bands of O_2 have been observed *during* electron bombardment of O_2 samples in krypton and xenon.[22] However, on the basis of the available evidence we cannot rule it out as an alternative explanation.

Sulfur atoms

Controlled warmup of matrices containing H_2S molecules, which had been subjected to mercury-arc photolysis during the deposition process, produced intense emissions which were identified as $S_2(B\,^3\Sigma_u^-\rightarrow X\,^3\Sigma_g^-)$, the sulfur equivalent of the Schumann–Runge bands of O_2. This same emission system has recently been observed in analogous warmup experiments of photolyzed (VUV) argon matrices containing OCS[4,5,7] and CS_2.[7] In these studies the source of the luminescence was attributed to the radiative recombination of ground state sulfur atoms. This is also believed to be the predominant radiative process in the present investigation, although a somewhat more complex mechanism must account for the initial generation of atomic sulfur.

Gaseous hydrogen sulfide exhibits a continuous absorption spectrum[25–30] over the 180–270 nm region with a broad maximum centered at ~190 nm. In the 200–255 nm region all available photochemical evidence[31] suggests that H_2S is decomposed, in the initial photochemical act, into hydrogen atoms and hydrosulfide radicals

$$H_2S+h\nu\rightarrow H+SH\,. \qquad (2)$$

Consequently, in the matrix experiments reported here, where photolytic wavelengths greater than 220 nm (mercury arc) were employed, Reaction (2) must be the primary photochemical process. The SH radical formed in this fashion can undergo further photolysis at these wavelengths to produce atomic hydrogen and sulfur. Although the first excited state of SH is bound, Ramsay[32] had shown from a detailed analysis of diffuse rotational lines that strong predissociation occurs in the first vibrational level of the $^2\Sigma^+$ state (~310 nm) and established upper/lower limits of 92.7/66.3 kcal/mole for the ground state dissociation energy of SH. Our experiments strongly support the possibility of an SH radical formed in Reaction (2) subsequently undergoing secondary photodissociation to its atomic constituents.

The chief result of matrix warmup is an enhancement of the diffusion of ground state sulfur atoms, some of which recombine in the following radiative fashion:

$$S(^3P)+S(^3P)+M\rightarrow S_2(B\,^3\Sigma_u^-,\ \nu'=0)+M\,. \qquad (3)$$

This is certainly feasible on energetic grounds if one considers the exothermicity of the recombination (102.5 kcal/mole)[33] with the energy of the B state in its ground vibrational level [T_0(Ar matrix) = 89.6 kcal/mole].[15] A similar S-atom recombination mechanism was proposed by Fair and Thrush[34,35] to account for the chemiluminescence observed in the gas phase reaction of H atoms with H_2S molecules.

The $B\rightarrow X$ emission system of molecular S_2 has been produced by a variety of methods. It has been generated by ultraviolet[15,36–38] and laser[39] excitation of sulfur components, as well as by electron bombardment[40,41] and shock heating.[42,43] It has also been observed as chemiluminescence in flames containing CS_2+O_2[44] and sulfur vapor[45,46] and more recently in SF_6 afterglows[47] and crossed molecular beams.[48] In the majority of these latter systems, where sulfur atoms are present, the $S_2(B\rightarrow X)$ emission is very likely produced by $S_2(B\,^3\Sigma_u^-)$ formed by S-atom recombination. Unfortunately, however, the $B\,^3\Sigma_u^-$ state does not correlate with two $S(^3P)$ atoms. In order to overcome this difficulty an inverse predissociation mechanism is proposed[34] where the $B\,^3\Sigma_u^-$ state is populated by a scheme in which two $S(^3P)$ atoms combine along a potential energy surface and make a radiationless transition (curve crossing) to the $B\,^3\Sigma_u^-$ state. The predissociating state which crosses the $B\,^3\Sigma_u^-$ potential curve and correlates with $S(^3P)+S(^3P)$ has been identified by Ricks and Barrow,[49] from S_2 dissociation studies, as a 1_u state:

$$S(^3P)+S(^3P)\xrightarrow{M}S_2(1_u)\xrightarrow{M}S_2(B\,^3\Sigma_u^-,\ \nu'=0)\,. \qquad (4)$$

This latter mechanism (4) is believed to be primarily responsible for the observation of $S_2(B\rightarrow X)$ emission in the H_2S-photolysis-warmup experiments in argon and krypton matrices.

The growth of the SO_2 phosphorescent emissions at the higher warmup temperatures (>26 °K) in the H_2S-photolysis experiments is believed to arise from the enhanced reaction of sulfur atoms with traces of molecular O_2 impurity

$$S(^3P)+O_2\rightarrow SO_2(a\,^3B_1\rightarrow X\,^1A_1)\,. \qquad (5)$$

It has been shown[50] that O_2 diffusion in a vapor-deposited argon matrix at 33 °K is appreciable. In the present investigation this was confirmed in the O_2-doped H_2S matrix experiments where only those emission features attributable to $SO_2(a\rightarrow X)$ phosphorescence were observed (Table III, Fig. 4). While the exact mechanism of chemiluminescence is not known, a recent gas-phase kinetic study[51] reports an Arrhenius activation energy of 0.00±0.10 kcal/mole for the $S(^3P)+O_2$ reaction, which is believed to proceed by the following path:

$$S(^3P)+O_2 \to [SOO]^\ddagger \to SO+O(^3P)\,. \tag{6}$$

The exact structure of the highly energized transition state $[SOO]^\ddagger$ remains uncertain[52] although the lack of any pressure dependence for the Reaction (6) was taken as evidence that the $[SOO]^\ddagger$ species is very short lived ($<10^{-10}$ sec). In a matrix, however, the cage effect[53,54] may prevent a considerable fraction of the SO + O fragments from escaping from each other [Reaction (6) is only ~ 5.6 kcal/mole exothermic]. As a result, it is probable that a sizable proportion of the SO + O products recombine in the inert gas cage to produce an excited SO_2 molecule

$$O(^3P)+SO+M \to SO_2^*+M\,, \tag{7}$$

$$SO_2^* \xrightarrow{M} SO_2(a\,^3B_1 \to X\,^1A_1)\,. \tag{8}$$

In the gas phase at low pressure the SO_2 afterglow has been shown to occur by Reaction (7).[55-57] The afterglow emission originates from three excited states of SO_2,[56] which is understandable in view of the high exothermicity (~ 132.1 kcal/mole) of Reaction (7). However, in the solid phase[58] or in a low temperature matrix[16] rapid $S_1 \to T_1$ intersystem crossing leads to phosphorescence ($a \to X$). On this basis, therefore, we conclude that the SO_2 phosphorescence observed on warmup of photolyzed matrices containing H_2S+O_2 molecules proceeds via the diffusion-controlled reactions (6)–(8), where the solid matrix cage enhances the O + SO chemiluminescent recombination reaction.

$O(^3P)+H_2S$

The dominant component of the emission spectrum observed upon warmup of a photolyzed codeposit of separate $Ar/O_3+Ar/H_2S$ matrix samples has been identified from photographs[2] as SO_2 phosphorescence ($a\,^3B_1 \to X\,^1A_1$). This was confirmed in the present experiments when a comparison of the emission band maxima (labeled A in Table IV) with earlier SO_2 matrix phosphorescence (uv-excited) results[17] revealed an average frequency difference of $23\pm10\ \mathrm{cm}^{-1}$.

It has likewise been shown from earlier infrared results[2] that the primary matrix processes following short-term photolysis after deposition are (a) photodecomposition of O_3 to generate O atoms and molecular oxygen and (b) subsequent O-atom diffusion and reaction with an isolated H_2S molecule in the following fashion:

$$\{O(^3P)+H_2S \to [H_2S=O]^\ddagger \to HSO+H \text{ or } H_2+SO\}_{\text{cage}}\,. \tag{9}$$

As demonstrated in the present O-atom/chemiluminescence experiments in argon matrices, there are appreciable quantities of trapped atomic oxygen, produced by the *in situ* matrix photolysis of O_3, which subsequently undergo enhanced diffusion upon warmup. Some of these oxygen atoms eventually encounter a nearby H_2S molecule and react, with little or no energy of activation, according to Eq. (9). Secondary O-atom attack on an SO or HSO fragment can then yield SO_2 in some initial excited state which evidently intersystem crosses to the $a\,^3B_1$ level and phosphoresces ($a \to X$). The most probable origin of the SO_2 phosphorescence, observed after warmup, is the O + SO reaction, although on energetic grounds the O + HSO reaction cannot be ruled out as a possible chemiluminescence source. In the $O+H_2S$ gas phase reaction, however, the kinetic data[59] favor the O + SO chemiluminescent route.

As mentioned earlier, the exact origin(s) of the *B* and *C* emissions (Table IV) are not presently known. However, they are clearly not attributable to either $O_2(A\,^3\Sigma_u^+ \to X\,^3\Sigma_g^-)$ or $S_2(B\,^3\Sigma_u^- \to X\,^3\Sigma_g^-)$. Moreover, the possibility of the emitting state being assigned to $SO(B\,^3\Sigma^-)$, $SH(A\,^2\Sigma^+)$, or $OH(A\,^2\Sigma^+$, Meinel bands) was ruled out (in some cases) on the basis of their high energy content [for $SO(B\,^3\Sigma^-)$ T_0 > exothermicity of Reaction (9)] as well as their known emission spectra[60] and ground state vibrational spacings [ω_e(SH, OH) ~ 2690, 3735 cm^{-1}, respectively]. Consequently, by elimination the most likely candidates responsible for this emission are the excited species HSO^*/H_2SO^* and/or a new emitting state of the SO molecule. In a recent account of the chemiluminescence observed in the gas phase $SH+O_3$ reaction Becker and co-workers[61] had assigned an emission spectrum in the 520–960 nm region to the $^2A' \to {}^2A''$ transition of an HSO radical. In the HSO spectrum only the ν_3 vibrations (S = O stretch) appeared to be involved in the ν' progressions with $\nu_3'' = 1013\pm5$ and $\chi_{33}'' \sim 6\ \mathrm{cm}^{-1}$ which agree with our approximate spacings (~ 1040 cm^{-1}). Energetically, it is possible to populate the $HSO(^2A')$ state by the $O+H_2S$ reaction. T_0(HSO) was experimentally determined to be 14 367 cm^{-1} (41 kcal/mole),[61] while the bond dissociation energy of an S–H bond in a hypothetical H_2SO molecule can be estimated by means of the following approximation based on a self-consistent field calculation[62] of the S–H bond overlap populations:

$$D(\text{H–HSO}) \approx D(\text{H–SH}) \times \frac{0.1509}{0.4853} = 28\ \text{kcal/mole}$$

taking $D(\text{H–SH}) = 89$ kcal/mole as derived from a recent photoionization study.[63] The energy content of a nascent H_2SO molecule, formed in the association Reaction (9), has been approximated[2] at 110 kcal/mole, which is more than sufficient to break an S–H bond in a hypothetical H_2SO molecule and populate the $^2A'$ state of HSO($\geq 28+41$ kcal/mole). However, in order to corroborate the absolute emission frequencies of the gas-phase study with our results a rather large gas-matrix blue shift (~ 4000 cm^{-1}) would have to be invoked. It is conceptually difficult to understand why such a large blue shift should occur and, for this reason, we cannot unambiguously assign either of the emission systems (*B* or *C*) recorded in our $O+H_2S$ matrix experiments to HSO radical chemiluminescence. The possibility of ascribing either or both of these emissions to an excited H_2SO^* species is an attractive alternative. However, virtually no information is available on such an excited state species. The similarity of the experimentally determined spacings in the *B* and *C* systems ($\omega \sim 1040\ \mathrm{cm}^{-1}$) to the ground state vibrational spacings of the SO molecule ($\omega_e \sim 1148\ \mathrm{cm}^{-1}$)[60] compels us to consider it as a likely emitter. However, if such is the case, then a new emission system of SO would have to be invoked since the present data cannot be corroborated with the known emission spectrum[60] of the SO molecule. Consequently, further experiments are now underway on the $O+H_2S$ chemiluminescent matrix reaction in an effort to resolve this question and more detailed discussion on this new type of reaction will be made in future publications.

Matrix effects

The influence of the matrix environment on the chemiluminescent emission spectra can be classified into two general types: diffusion effects and guest–host interactions. In the close-packed lattices of the solid inert gases the size of both the substitutional and interstitial vacancies increases with increasing atomic weight. If the size of a lightweight guest molecule is comparable to these vacancies, appreciable diffusion may occur, depending, of course, on the rigidity of the lattice (temperature). In the present investigation this was evident in those warmup experiments involving O_3-containing matrices after initial photolysis. The Herzberg I emission system $(A \rightarrow X)$ of molecular oxygen, produced as a consequence of O-atom recombination in the matrix, was notably intense in solid argon, much less so in krypton, and undetectable in xenon matrices. This can be accounted for by the increased diffusion of atomic oxygen in the heavier inert gas matrices (Kr, Xe) *during* the O_3-photolysis step (temp. ~8 °K) which ultimately leads to appreciable O-atom recombination *before* warmup. Such was not the case for the sulfur atom reactions. However, the *mass* × *radius* product of atomic sulfur is more than four times that of atomic oxygen, and therefore diffusion would not be expected to be as great. From a structural point of view it is observed that the atomic diameter of oxygen (~1.2 Å) is approximately equal to or slightly less than the average interstitial site diameter $[1/2 \times (O_h + T_d)]$ of solid krypton (1.28 Å)[64] although significantly less than that of solid xenon (1.39 Å) at ~4 °K. This is not the case for sulfur whose larger atomic diameter (2.54 Å), as well as increased mass, would hinder its diffusion in all three matrices prior to warmup. It therefore becomes apparent that both the relative size and mass of a diffusing species, such as an atom, must be taken into account prior to the diffusion-controlled warmup procedure.

The nature of the guest–host interaction and its influence on the matrix chemiluminescence spectrum is a considerably more complex subject. In the S_2-chemiluminescence experiments the structured emission recorded in argon and krypton matrices was observed only as a broad, relatively unresolved band in the xenon experiments. Such enormous line broadening suggests a number of causes. One possibility, which was considered early on, was the likelihood of vibrationally unrelaxed emission. In a xenon matrix, where the substitutional site is large (4.34 Å diam.), two sulfur atoms may recombine during the warmup process to eventually produce an excited S_2 molecule whose physical dimensions $[\sigma(^3\Sigma_u^-) \sim 4.2 \text{ Å}]$[60] may be less than that of a substitutional site. If the radiative lifetime is small compared to site migration and the collisional frequency of a host in a cage, the higher excited state vibrational levels $(\nu' \leq 9)$[34] may not be sufficiently quenched and hence contribute to the overall emission spectrum (i.e., pseudo-gas phase). The absence of low frequency vibrations and the short radiative lifetime of S_2(45.0 ± 0.6 nsec)[65] suggests that fluorescence $(B\,^3\Sigma_u^- \rightarrow X\,^3\Sigma_g^-)$ might be competitive with vibrational relaxation rates. In the most recent study[65] of the lifetime of the $B\,^3\Sigma_u^-$ state of S_2 the authors themselves conclude, from an apparent lack of dependence of the $B\,^3\Sigma_u^-$ lifetime on the vibrational energy of the excited state, that this state is only weakly perturbed, so that the rate of nonradiative transitions is still much smaller than the radiative transition rate. Moreover, Brewer and Brabson, in their pioneering S_2-fluorescence study,[15] had observed the $(1, \nu'')$ progression in $S_2(B \rightarrow X)$ emission in xenon matrices excited with 289.4–313.2 nm light. In the present case a superposition of the $n+1$ Franck–Condon emission maxima from each of the excited ν_n' levels would have the overall effect of broadening the $S_2(B \rightarrow X)$ emission spectrum towards the blue. This would not seem to be the case for argon and krypton matrices where the substitutional site diameters are smaller [3.76 Å (Ar), 3.99 Å (Kr)] and collisional quenching of any vibrational excitation apparently predominates.

Alternative explanations for such fluorescent line broadening might include the possibility of S_2^*–Xe van der Waals "complex" formation with subsequent radiative decay to an unbound or weakly bound ground state, or, as a consequence of the increased ionic character of the excited state (i.e., S_2^-–Xe^+), the activation of other transitions in S_2 via dipolar enhancement of the appropriate transition moments. A polarizable atom like xenon can enhance dative bond formation which, in principle, is more important in electronically excited diatomics than ground state diatomics. Recent *ab inito* configuration-interaction calculations[66] on the states of the rare gas monoxides have demonstrated a strong enhancement of the $2'\,\Sigma^+$–$1'\,\Sigma^+$ transition moment ("green bands" in XeO) in the sequence Ar < Kr < Xe because of the increase in the ionic character in the $1'\,\Sigma^+$ state in the same sequence. As to whether the line broadening observed in the chemiluminescent reactions of sulfur atoms in xenon matrices is, in fact, attributable to unrelaxed vibrational emission and/or xenon-interaction effects, we can only speculate on the basis of the available evidence.

CONCLUSIONS

Diffusion-controlled warmup (8 → 20 °K) of separate, photolyzed inert gas matrices (Ar, Kr, Xe) containing O_3, H_2S+O_2, and O_3+H_2S molecules produced intense chemiluminescence in the visible spectral region. In each case the resultant emission spectrum was dispersed and analyzed by an optical multichannel technique which enabled simultaneous parallel detection across an extensive wavelength region [~275 Δ(nm)] during the matrix diffusion processes. Long vibrational progressions were observed in each spectral system.

Ground state atomic oxygen $O(^3P)$ was observed to recombine in solid argon matrices, at temperatures of the order of ~ 17 °K, to produce the intense Herzberg I band system of molecular $O_2(A \to X)$ which was also observed in krypton although not in xenon matrices. The lack of any detectable emission in xenon matrices is interpreted as being due to appreciable diffusion and eventual recombination of atomic oxygen before the warmup process and its associated enhancement of diffusion.

Analogous matrix experiments with sulfur atoms, generated by *in situ* photolysis of H_2S, produced intense S_2 fluorescence $(B \to X)$ in all three matrices (Ar, Kr, Xe). Long structured vibrational progressions $(0, v'')$ were observed in argon and krypton matrices, while a broad, relatively structureless emission was observed in xenon (365–532 nm). The exact origin of the line broadening in xenon is not known with certainty, although possible mechanisms might include such processes as vibrationally unrelaxed fluorescence and/or S_2^*-Xe van der Waals complex formation. The presence of small amounts of O_2 impurity was observed to produce the SO_2 phosphorescence spectrum $(a \to X)$ which appeared to be orders of magnitude more intense than the S_2 fluorescent emissions.

The matrix reactions of ground state sulfur atoms $S(^3P)$ with O_2 molecules is believed to proceed via O-atom abstraction by atomic sulfur, followed by cage recombination of the fragments $(O + SO)$ to produce electronically excited SO_2 which subsequently (via intersystem crossing) phosphoresces. The emission spectrum, observed in the general wavelength region of 390–520 nm, consisted of the intense vibrational progression $a(0,0,0) \to X(v_1'', v_2'', 0)$.

Controlled warmup, after short-term photolysis, of dilute argon matrices containing O_3 and H_2S molecules produced the SO_2 phosphorescence spectrum $(a \to X)$ and two emission systems of lower intensity (520–675 nm), each with an approximate vibrational spacing of ~ 1040 cm^{-1}. The electronically excited SO_2 is believed to be formed by O-atom attack on the SO and/or HSO fragments generated in the initial $O + H_2S$ matrix reaction

$$O + H_2S \to [H_2SO] \to HSO + H \text{ or } H_2 + SO .$$

The origin of the two less intense emission systems is not presently known although a list of likely candidates would include such excited state species as HSO^*/H_2SO^* and/or a new emitting state of SO. Further experiments on the $O + H_2S$ matrix reactions are under way in an effort to provide some clues concerning the nature of the emitter(s) responsible for this chemiluminescence.

Note added in proof: Since the submission of this manuscript, a detailed examination of selectively-excited O_2 molecules in inert gas matrices [J. Goodman and L. E. Brus, J. Chem. Phys. **67**, 1482 (1977)] had analyzed the O_2 emission, formerly attributed to $A \to X$ fluorescence, in terms of $C\,^3\Delta_1 \to X\,^3\Sigma_g^-$ and $c\,^1\Sigma_u^- \to a\,^1\Delta_g$ transitions for argon-matrix isolated $^{16}O_2$ and $^{18}O_2$, respectively. The emission wavelengths reported in that study for $^{16}O_2$ in argon are in general agreement with warm-up observations of photolyzed argon matrices containing $^{16}O_3$ molecules.

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