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Reactions of Germanium Vapor with Oxidizers: Photon Yields and a New GeO Band System

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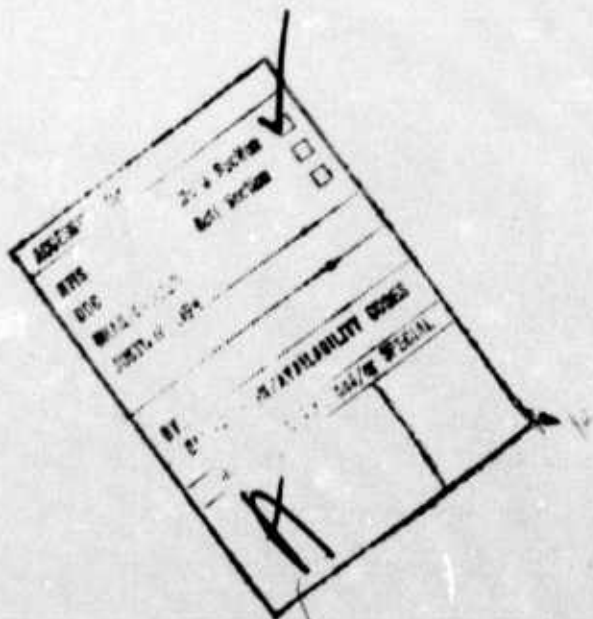
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FOR THE COMMANDER

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band systems were measured to be small ($<0.1\%$ in all cases) and to be strongly pressure dependent in the 0.5 to 20 Torr region. Reaction of Ge vapor with F_2 produced $GeF(A^2\Sigma^+ \rightarrow X^2\Pi)$ chemiluminescence with a measured photon yield of 6.8×10^{-4} ; the flames from $Ge + Br_2$ and $Ge + Cl_2$ were too weak to measure.

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PREFACE

Discussions with Dr. R. W. Field and Dr. B. G. Wicke have been of great value, and the hospitality of Dr. H. P. Broida is especially acknowledged. This research was partially supported by the Air Force Office of Scientific Research under Grant No. AFOSR-74-2724.

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I. INTRODUCTION

Spectroscopic studies of the chemiluminescent reactions of metal vapors have been receiving increased attention recently, since such reactions have been shown to warrant investigation as potential chemical laser systems.¹ Often, the chemiexcitation of diatomic metal oxides and halides is very selective, in a manner that permits spectroscopic observation of the lowest-lying molecular states. We report here the chemiluminescence spectra and photon yields of three electronic band systems that involve the lower-lying states of the GeO molecule, including a previously unidentified intercombination band system.

Previous investigations of the absorption^{2,3} and emission⁴⁻⁶ spectra of GeO in the 225- to 332-nm uv region established the vibrational analysis of a red-degraded band system, designated as the A-X system (known earlier in the literature as D-X). From an initial rotational analysis⁷ of this system, it was concluded that the transition involved was $^1\Sigma - ^1\Sigma$. However, recent high-resolution rotational analyses⁸⁻¹⁰ of several bands of the A-X system have established that the transition is in fact $^1\Pi - ^1\Sigma^+$. This A-X transition is analogous to the Fourth Positive system of the homologous CO molecule.

In further analogy with the band spectra of the Group IVA diatomic oxides¹¹ (CO, SiO, GeO, SnO, and PbO), additional GeO band systems in the visible spectral region are expected. Indeed, in several previous studies of GeO, blue emission was observed and attributed to transitions involving

molecular states that are lower lying than $A^1\Pi$. The spectrum of the blue chemiluminescence produced during the gas phase reaction of GeH_4 (germane) with atomic oxygen contained many bands extending from 245 to 500 nm.¹² In addition to 76 bands identified as belonging to the A-X system of GeO, 26 unidentified bands between 300 and 380 nm indicated the strong possibility of a new band system of GeO in the 300- to 500-nm region. The spectrum of matrix-isolated GeO showed a matrix-induced blue phosphorescence as well as strong $A \rightarrow X$ uv absorption.¹³ The phosphorescence was assigned to $^3\Pi \rightarrow X^1\Sigma^+$ emission, analogous to the Cameron band system of CO.¹⁴ The thermal emission spectrum of GeO produced from the reaction of Ge vapor with air at 2400°C was observed in the 460- to 510-nm region; a red-degraded band system in this region was vibrationally analyzed to yield a single molecular state of GeO with $T_e = 21\,117\text{ cm}^{-1}$.¹⁵ The term symbol designation for this state was unassigned. In an experiment more closely related to that reported here, the chemiluminescent reaction of Ge atoms with N_2O was studied by emission spectroscopy.^{16,17} The Ge atoms were produced in a hollow cathode discharge of 1% GeH_4 in He, and the spectra were obtained with a gas-phase flow reactor. A red-degraded band system involving the ground state of GeO was observed in the 375- to 525-nm visible region, and the vibrational analysis located the upper state of the transition at $T_e = 27\,731\text{ cm}^{-1}$. On the basis of indirect evidence, the authors concluded that the emission was from a $^3\Sigma^+$ state, analogous to the Hopfield-Birge band system of CO. The agreement between bandhead positions and relative intensities indicated that the upper state in this gas phase chemiluminescence was the same as that observed¹³ in the matrix isolation phosphorescence experiment.

In the present experiments, we have observed the chemiluminescence from reactions of ground state atomic Ge vapor with several oxidants, including N_2O , NO , NO_2 , O_2 , Br_2 , Cl_2 , and F_2 . We began this study in order to measure quantitatively the photon yields of such chemiluminescent reactions. From the analysis of the resultant chemiluminescent flames in the oxide systems, we also hoped to obtain a better characterization of the lowest-lying electronic states of GeO , since some confusion existed from the previous studies on this molecule.

II. EXPERIMENT

Our experiments were carried out in a metal atom flow system described in detail elsewhere.¹⁸ Molten Ge was vaporized from an alumina crucible heated to 1380 to 1460°C, at which temperature Ge is known to vaporize almost entirely as atomic species.¹⁹ The metal vapor, entrained in a flow of Ar or He carrier gas, was then mixed with an oxidizing gas several centimeters above the crucible in order to form a well-defined chemiluminescent flame. Several light baffles placed between the crucible and the mixing region shielded the observation volume from excessive black-body furnace radiation. The flames were studied at carrier gas pressures from 0.5 to 20 Torr, with estimated linear flow rates near 10^3 to 10^4 cm-sec⁻¹. Metal flow rates were typically 2×10^{17} to 9×10^{17} atoms/sec; estimated concentrations entering the reaction zone were on the order of 10^{14} atoms/cm³ at 10 Torr total pressure.

Spectra were obtained with a 1-m Czerny-Turner scanning monochromator equipped with appropriate photomultiplier tube-grating combinations to extend the detection range from 190 to 1100 nm. Atomic pen lamp reference lines were used for absolute wavelength calibration. Measurements of individual bandheads in the spectra were made with 0.05- to 0.08-nm resolution.

Absolute photon yield measurements were determined by comparison of the signal intensity from the flames with that of a quartz-iodine tungsten lamp of known output intensity. From such a comparison, the total number

of photons per second emitted by the flame in a given spectral region could be calculated quantitatively.²⁰ This number was then divided by the number, N , of Ge atoms reacting per second to determine the photon yield. With the assumption that all of the vaporized metal atoms underwent reaction with the oxidizer gas, which was virtually assured by the use of excess oxidant, the quantity N was determined by the weight loss of the Ge from the crucible at the conclusion of the experiment. Throughout the experiment, the intensity of one particular chemiluminescent emission band was monitored to ensure that the metal atom flow rate remained approximately constant.

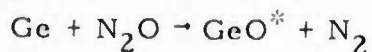
III. RESULTS

A. Chemiluminescent Spectra of the Oxide Systems

A chemiluminescent flame attributable to emission from electronically excited GeO was produced when Ge vapor was reacted with N₂O, NO, NO₂, or O₂; no other molecular emission was observed. With N₂O, the flame appeared deep blue, but with O₂ it was nearly invisible to the eye. In all cases, the visible chemiluminescence was a flame confined well within the observation boundaries of the detection system. The chemiluminescence from the reactions with NO₂ and NO was similar to that from N₂O and O₂, respectively, but weaker in intensity.

Figure 1 shows the Ge plus N₂O chemiluminescent spectrum at 1 Torr total pressure of Ar carrier gas. The analysis obtained has shown that the spectrum consists of three distinct band systems of GeO, all terminating in the X ¹Σ⁺ ground state.

In the uv region between 236.5 and 310.5 nm, the A ¹Π - X ¹Σ⁺ system was observed. The exothermicity of the chemiexcitation reaction



is 5.13 eV and is sufficient to produce GeO (A ¹Π). The wavelengths of 28 bandheads were measured, and the results were generally in agreement with the previously determined^{3, 5} A-X bandhead positions to within 0.03 nm.

Table I contains the complete array of the A-X bands observed. The highest

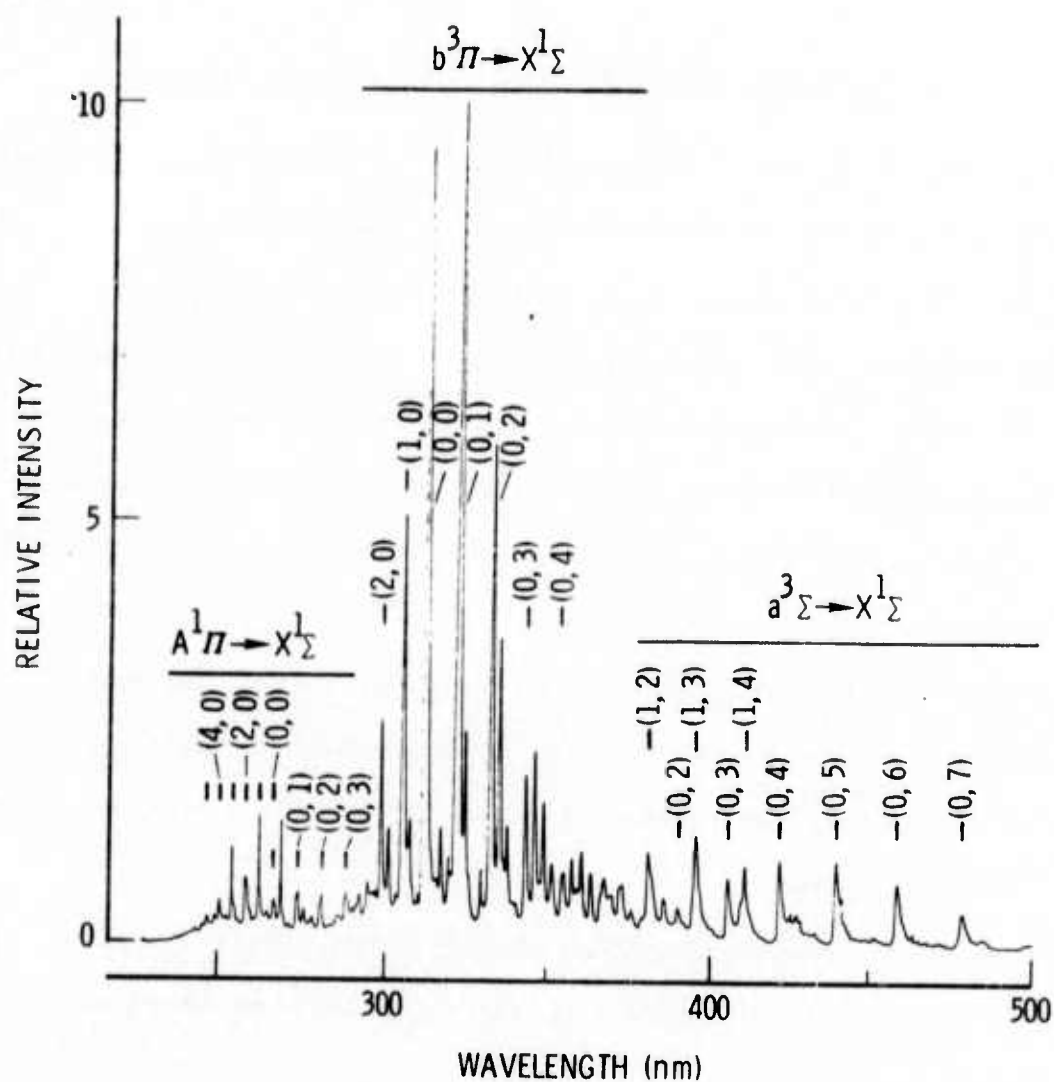


Fig. 1. Spectrum of Ge + N₂O chemiluminescence between 215 and 500 nm. Total pressure is ~1 Torr. No correction has been made for instrument response.

TABLE I. Deslandres table of the $^{74}\text{GeO A } ^1\Pi - X^1\Sigma$ bandheads observed in the $\text{Ge} + \text{N}_2\text{O}$ chemiluminescent reaction (28 bandheads were measured).

ν''	0	1	2	3	4	5	6	7	8	9
0	265.96(5) ^a 37 588(8) ^b 0.0554 ^c	273.01(2) 36 618(3) 0.1627	280.43(3) 35 649(4) 0.2386	288.17(2) 34 692(2) 0.2303	296.28(4) 33 742(5) 0.1630	-	-	-	-	-
1	261.40(2) 38 244(3) 0.1523	268.31(2) 37 259(3) 0.1931	275.45(3) 36 294(4) 0.0631	-	290.79(2) 34 379(2) 0.0778	d	d	316.55(5) 31 581(5) 0.1078	0.0146	0.0045
2	257.18(2) 38 872(3) 0.2179	263.80(5) 37 896(7) 0.0675	-	278.00(2) 35 961(3) 0.1141	285.56(4) 35 009(5) 0.0746	-	-	310.42 32 205(5) 0.1292	d	328.94(5) 30 392(5) 0.1042
3	253.10(2) 39 498(3) 0.2150	-	266.26(3) 37 546(4) 0.1048	d	-	d	d	-	-	d
4	249.20 40 116(5) 0.1639	-	-	-	0.1115	0.0933	0.0613	0.0004	0.0461	0.1226
5	245.44(3) 40 731(5) 0.1023	251.54(5) 39 743(8) 0.1210	0.0486	0.0065	0.0878	0.0215	0.0220	0.0877	0.0412	0.0008
6	241.93(3) 41 322(5) 0.0541	247.76(2) 40 349(3) 0.1447	0.0087	0.0744	0.0274	0.0278	0.0716	0.0035	0.0418	0.0793
7	238.50(5) 41 916(9) 0.0247	244.15(2) 40 946(3) 0.1193	d	-	-	-	-	-	-	-
8	-	240.70(5) 41 533(9) 0.0765	0.0769	0.0119	0.0631	0.0126	0.0430	0.0368	0.0087	0.0643
9	-	-	d	-	0.0575	0.0128	0.0521	0.0033	0.0584	0.0047
10	0.0034	0.0401	0.1154	0.0597	0.0095	0.0578	0.0033	-	0.0100	0.0343
11	0.0010	0.0176	0.0825	0.1047	0.0073	0.0453	0.0195	0.0335	0.0164	0.0403
	-	-	236.50(4) 42 270(7) 0.0468	d	-	-	-	-	-	-
	0.0002	0.0065	-	0.1086	0.0544	0.0054	0.0533	0.0000	0.0492	0.0000

^aWavelengths (nm) in air, with estimated standard deviation of the measurement given in parentheses.

^bCorresponding wave number (cm^{-1}) in vacuum and estimated error.

^cCalculated Franck-Condon factor for the transition (see text).

^dBandheads are indicated in the spectrum but are too badly overlapped by stronger bands to obtain a measurement.

vibrational level observed in the $A^1\Pi$ state was $v' = 11$, which is very close to what would be predicted on the basis of the reaction exothermicity.

Between 273.7 and 379.3 nm, a second system consisting of 33 sharp, red-degraded bands was observed. Vibrational assignments were made by fitting the bands into a Deslandres table, given in Table II. Under the assumption that the heads are close to the band origins, the wavelengths of the 33 bands were fit to the equation

$$\nu = T_e + \omega'_e(v' + \frac{1}{2}) - \omega_e x'_e(v' + \frac{1}{2})^2 - \omega''_e(v'' + \frac{1}{2}) + \omega_e x''_e(v'' + \frac{1}{2})^2 \quad (1)$$

with a weighted least squares fit method. The weight assigned to an individual band position was equal to the inverse of the estimated standard deviation of the wavelength measurement. Contributing to the uncertainty of a bandhead measurement is the natural distribution of Ge isotopes. The relative abundances of the five known isotopes ^{74}Ge , ^{72}Ge , ^{70}Ge , and ^{76}Ge are 37.1, 27.3, 21.2, 7.9, and 6.5, respectively. If we ignore the bandheads that are due to ^{73}GeO and ^{76}GeO , the bands of ^{72}GeO and ^{70}GeO will have about 0.74 and 0.57, respectively, of the intensity of the corresponding bands of the most abundant molecule ^{74}GeO . This was taken into account when bandhead measurements were made, and we assign the bands in Table II to ^{74}GeO . Molecular constants derived from the least squares fit are given in Table III. All of the bandhead wave numbers calculated from these constants agree to within better than 8 cm^{-1} of the experimental measurements, and the weighted root-mean-square deviation of the fit is 1.3 cm^{-1} . The values of

TABLE II. Deslandres table of the $^{74}\text{GeO b } ^3\Pi - X ^1\Sigma$ bandheads observed in the $\text{Ge} + \text{N}_2\text{O}$ chemiluminescent reaction (33 bandheads were measured).

v'' v'	0	1	2	3	4	5	6	7	8	9
0	312.36(2) ^a 32 005(2) ^b 0.2935 ^c	322.17(2) 31 031(2) 0.3589	332.55(3) 30 062(3) 0.2229	343.54(2) 29 100(2) 0.0906	355.16(6) 28 148(5) 0.0267	-	-	-	-	-
1	305.40(2) 32 734(3) 0.3546	- 0.0149	324.72(2) 30 787(2) 0.1041	335.14(2) - 0.2352	346.20(2) 28 877(2) 0.1796	357.88(2) 27 934(2) 0.0801	370.20(6) 27 005(4) 0.0246	-	-	-
2	298.94(2) 33 442(2) 0.2212	307.93(4) 32 465(4) 0.1005	317.43(3) 31 494(3) 0.1395	- - 0.0001	337.94(3) 29 583(3) 0.1229	349.06(3) 28 640(2) 0.2013	360.82(6) 27 707(5) 0.1371	373.20(6) 26 788(4) 0.0568	-	-
3	292.69(4) 34 156(5) 0.0933	301.37(3) 33 172(3) 0.2258	- - 0.0001	319.95(3) 31 246(3) 0.1396	d - 0.0456	-	351.80(5) 28 417(4) 0.1555	363.60(5) 27 502(4) 0.1716	d -	-
4	- 0.0291	295.21(3) 33 864(3) 0.1791	303.94(5) 32 892(4) 0.1121	- - 0.0438	d - 0.0592	d	-	-	366.62(5) 27 268(4) 0.1670	379.33(5) 26 355(3) 0.1330
5	- 0.0069	- 0.0854	297.67(5) 33 584(6) 0.1924	- - 0.0206	- - 0.0971	-	d	-	-	d
6	- 0.0012	- 0.0280	291.89(5) 34 249(6) 0.1416	d - 0.1402	- - 0.0015	d	-	-	-	-
7	- 0.0001	- 0.0064	- 0.0639	d - 0.1698	- - 0.0673	-	-	-	-	-
8	- 0.0000	273.74(3) ^e 36 520(4) 0.0009	281.20(3) ^e 35 551(4) 0.0193	288.94(3) ^e 34 599(4) 0.1062	297.05(6) 33 655(7) 0.1586	-	-	-	-	-
9	- 0.0000	- 0.0000	- 0.0037	- 0.0418	- 0.1411	d	-	-	-	-
10	- 0.0000	- 0.0000	- 0.0003	- 0.0104	- 0.0724	d	-	-	-	-
							0.0640	0.0148	0.0550	0.0145

^aWavelengths (nm) in air, with estimated standard deviation of the measurement given in parentheses.

^bCorresponding wave number (cm^{-1}) in vacuum and estimated error.

^cCalculated Franck-Condon factor for the transition (see text).

^dBandheads are indicated in the spectrum but are too badly overlapped by stronger bands to obtain a measurement.

^eThese bands are interpreted as being present owing to perturbations with $A \frac{1}{2}$ ($v = 0$) (see text).

TABLE III. ^{74}GeO vibrational constants (cm^{-1}) of $b \rightarrow X$ near-uv system.^a

State	T_e	w_e	$w_e x_e$
b	$32\,132 \pm 2$	734.9 ± 3.6	5.30 ± 0.80
X^b	0	985.7 ± 2.0	4.32 ± 0.26

^aThe stated uncertainties represent two standard deviations.

^bThe vibrational constants for $X \ ^1\Sigma^+$ given in Footnote 8 are $w_e = 986.84$ and $w_e x_e = 4.47$.

ω_e'' and $\omega_e x_e''$ from Table III agree to within two standard deviations with the vibrational constants⁸ of the $X^1\Sigma^+$ state of ^{74}GeO , which indicates that the chemiluminescent near-uv emission terminates on the ground state of GeO. The value of ω_e' is 13% larger than the value for the $A^1\Pi$ state and is dissimilar to any ω_e value reported previously for molecular states that are lower lying than $A^1\Pi$. Thus, we are observing a new state of GeO, hereafter called the b state, with a T_e value of $32\,132\text{ cm}^{-1}$, which is $5\,634\text{ cm}^{-1}$ lower than T_e for the $A^1\Pi$ state.

Further into the visible region, between 326.3 and 557.9 nm, we observed 37 bands of a third GeO system. Measured bandhead wavelengths and vibrational assignments are given in Table IV. The measured bandheads indicate that this is the same system observed in the reaction of Ge (from GeH_4) with N_2O ^{16,17}; however, in the present study, emission has been observed from higher v' levels, up to $v' = 5$. Band positions were fit to (1) with the weighted least squares method, and the derived molecular constants are given in Table V. Calculated bandhead wave numbers agree with the experimental measurements to within better than 7 cm^{-1} ; the weighted root-mean-square deviation of the fit is 1.6 cm^{-1} . The upper state at $T_e = 27\,733\text{ cm}^{-1}$ is labeled the a state, as previous workers^{16,17} have done, while the ω_e'' and $\omega_e x_e''$ values indicate that the lower state is again $X^1\Sigma^+$.

The relative intensities of the $A \rightarrow X$, $b \rightarrow X$, and $a \rightarrow X$ emissions were observed to be dependent on the total pressure in the flow system and on the identity of the carrier gas. Variation with pressure of representative bands for each of the three band systems observed for $\text{Ge} + \text{N}_2\text{O}$ in Ar are shown

TABLE IV. Deslandres table of the ^{74}GeO a $^3\Sigma - X^1\Sigma$ bandheads observed in the $\text{Ge} + \text{N}_2\text{O}$ chemiluminescent reaction (37 bandheads were measured).

	0	1	2	3	4	5	6	7	8	9	10	11
0	-	376.13(3) 26 579(2) 0.0037	390.40(2) 25 608(1) 0.0692	405.59(3) 24 648(2) 0.1330	421.88(3) 23 697(1) 0.1839	439.31(2) 22 757(1) 0.1948	458.13(2) 21 822(1) 0.1643	478.41(5) 20 897(2) 0.1131	500.41(2) 19 978(1) 0.0648	524.19(2) 19 072(1) 0.0312	550.01(3) 18 176(1) 0.0128	-
1	354.71(4) ^a 28 184(3) ^b 0.0177 ^c	367.46(4) 27 206(3) 0.0754	381.07(2) 26 234(1) 0.1371	395.48(4) 25 279(3) 0.1295	410.97(4) 24 326(2) 0.0543	-	-	d	485.08(5) 20 609(2) 0.1438	507.46(4) 19 701(2) 0.1347	531.69(2) 18 803(1) 0.0935	557.94(3) 17 918(1) 0.0510
2	d	359.26(4) 27 827(3) 0.1214	372.20(3) 26 860(2) 0.1101	386.03(2) 25 897(1) 0.0221	400.6(3) 24 955(19) 0.0102	-	433.28(5) 23 073(3) 0.0872	451.35(5) 22 150(2) 0.0264	-	-	d	539.3(1) 18 537(3) 0.1318
3	339.7(2) 29 429(17) 0.0789	351.52(5) 28 440(4) 0.1240	363.93(5) 27 470(4) 0.0335	-	d	d	-	439.12(4) 22 766(2) 0.0432	457.4(1) 21 857(4) 0.0823	-	-	-
4	d	d	-	d	382.0(2) 26 170(14) 0.0497	0.0519	0.0001	-	-	0.0379	0.0000	0.0399
5	326.3(2) 30 638(18) 0.1283	336.94(6) 29 670(5) 0.0343	348.2(2) 28 711(16) 0.0256	360.1(2) 27 762(15) 0.0668	-	0.0004	0.0545	427.63(4) 23 378(2) 0.0540	0.0014	0.0342	0.0760	0.0358
					0.0013	0.0456	0.0451	0.0002	0.0495	0.0473	0.0004	0.0378

Wavelengths (nm) in air, with estimated

^aWavelengths (nm) in air, with estimated standard deviation of the measurement given in parentheses.

^bCorresponding wave number (cm^{-1}) in vacuum and estimated error.

^cCalculated Franck-Condon factor for the transition (see text).

^dBandheads are indicated in the spectrum but are too badly overlapped by stronger bands to obtain a measurement.

TABLE V. ^{74}GeO vibrational constants (cm^{-1}) of $a \rightarrow X$ visible system.^a

State	T_e	ω_e	$\omega_e x_e$
a	$27\,733 \pm 2$	633.3 ± 2.0	2.72 ± 0.58
X^b	0	987.6 ± 1.0	4.50 ± 0.08

^aThe stated uncertainties represent two standard deviations.

^bThe vibrational constants for $X \ ^1\Sigma^+$ given in Footnote 8 are $\omega_e = 986.84$ and $\omega_e x_e = 4.47$.

in Fig. 2. Total pressures in the range of 0.5 to 20 Torr were obtained by varying the pumping speed and the Ar flow so as to keep the signal intensity maximized; the N_2O flow was kept constant and very small (i.e., excess metal conditions) throughout the pressure-dependence measurements in order to eliminate the effects of any metal flow rate variations. Because of the overlapping of the $b \rightarrow X$ system with the red end of the $A \rightarrow X$ system and with the blue end of the $a \rightarrow X$ system, and because of the different pressure dependences of the three band systems, the apparent chemiluminescent spectrum changed with pressure. Thus, for example, at 1 Torr of Ar, the (2,1) band of $b \rightarrow X$ at 307.93 nm was easily observed, but at 10 Torr of Ar, a condition favoring decreased $b \rightarrow X$ and increased $A \rightarrow X$ intensity, the band observed in this region was the (1,6) transition of $A \rightarrow X$ at 307.51 nm.

Significant changes in the relative intensities of the three GeO band systems occurred upon changing the carrier gas from Ar to He. At 1 Torr pressure of carrier gas, the intensity of $a \rightarrow X$ emission increased by a factor of 15 with respect to $b \rightarrow X$ emission on changing from Ar to He; on the other hand, the $A \rightarrow X$ intensity decreased by a factor of 2 with respect to $b \rightarrow X$ for the same change in carrier gas. The ratio of $a \rightarrow X$ to $b \rightarrow X$ intensity from $\text{Ge} + \text{N}_2\text{O}$ in He remained constant upon increasing the total pressure from 1 to 3.5 Torr, while the weak $A \rightarrow X$ intensity increased by a factor of 2 relative to $b \rightarrow X$.

As mentioned earlier, the $\text{Ge} + \text{O}_2$ flame in Ar is nearly invisible to the eye because of the near absence of a $^3\Sigma^+ \rightarrow X\ ^1\Sigma^+$ emission. Its chemiluminescent spectrum at 1 Torr total pressure of Ar is shown in Fig. 3.

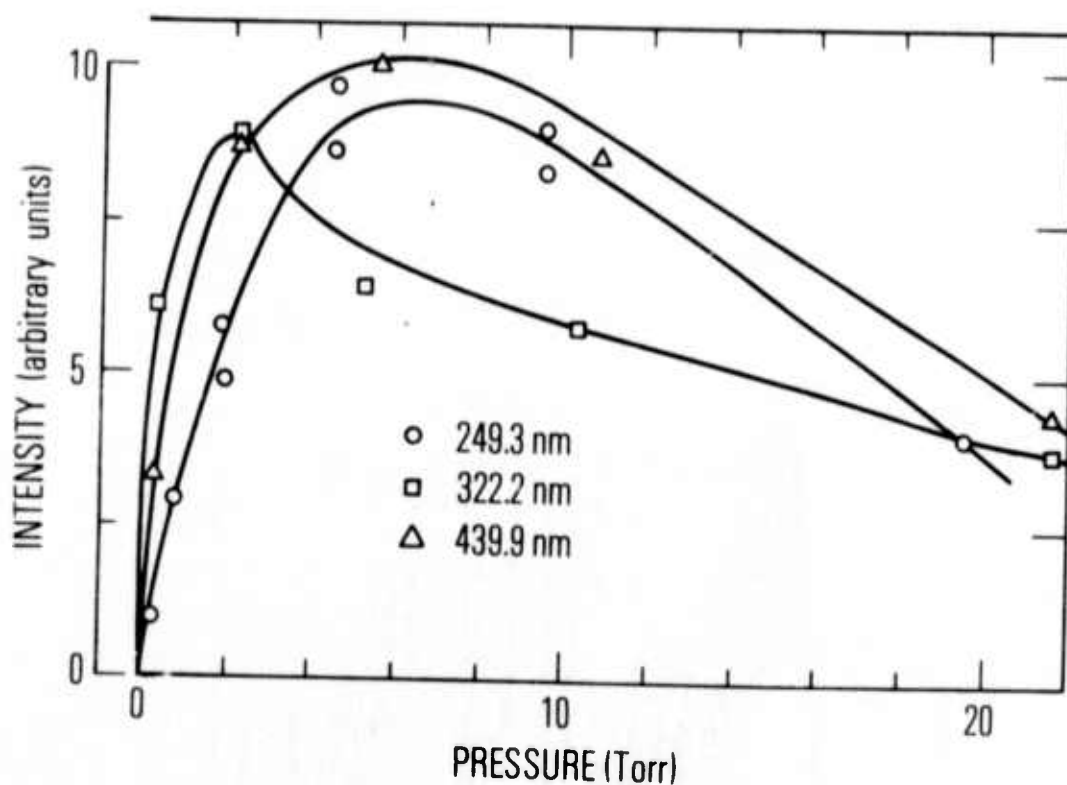


Fig. 2. Pressure dependence of A $^1\Pi \rightarrow$, b $^3\Pi \rightarrow$, and a $^3\Sigma^+ \rightarrow$ X $^1\Sigma^+$ band system emission, as represented by bands at 249, 322, and 440 nm, respectively, produced by the reaction of Ge with N₂O in Ar. The intensity distribution among bands within a system showed no large change over the range of pressures considered; hence, the individual bands are an excellent approximation to the behavior of the systems to which they belong.

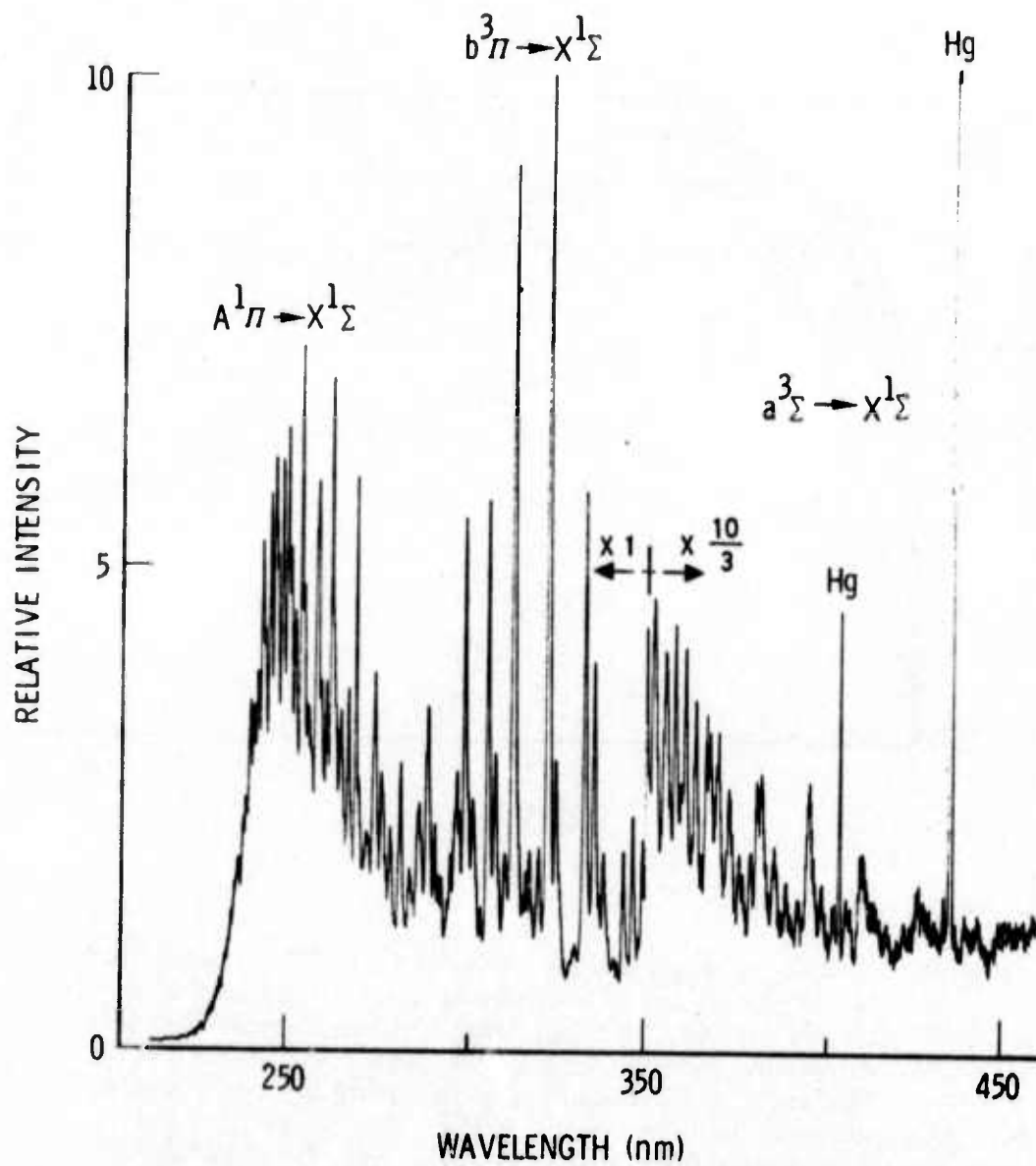
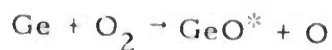


Fig. 3. Spectrum of Ge + O₂ chemiluminescence from 215 to 460 nm at a total pressure of 1 Torr, uncorrected for instrument response. The Hg lines are from room lights.

The exothermicity of the chemiexcitation reaction



is only 2.55 eV and is insufficient to produce any known excited state of GeO directly. The chemiluminescent spectra indicate, however, that GeO ($A^1\Pi$) is produced in greater amounts relative to the lower-lying a and b states than in the $\text{Ge} + \text{N}_2\text{O}$ reaction. The chemiexcitation in $\text{Ge} + \text{O}_2$ flames is apparently due to a multistep reaction process. The variation of the $A \rightarrow X$ and $b \rightarrow X$ systems with pressure, as measured in a metal-rich flame, is similar to the variation shown in Fig. 2 for $\text{Ge} + \text{N}_2\text{O}$, except that the peaks occur at lower pressures: ~ 2 Torr and ~ 0.5 Torr for $A \rightarrow X$ and $b \rightarrow X$, respectively.

B. Evidence for Perturbations in GeO ($A^1\Pi$)

Anomalous intensity distributions were observed in the (0, 1), (0, 2), (0, 3), and (0, 4) bands of the $A^1\Pi \rightarrow X^1\Sigma^+$ chemiluminescent emission from $\text{Ge} + \text{N}_2\text{O}$ in Ar at low pressures, near 1 Torr. It can be seen in Fig. 4 that a sharp increase in intensity for these bands occurs at wavelengths longer than expected from the previously measured⁵ bandheads. In each case, the sharp rise occurs $95 \pm 3 \text{ cm}^{-1}$ to the red of the respective bandhead. At higher pressures, near 10 Torr (see Fig. 5), the intensity distribution in each band in question moves toward the expected distribution with a sharp increase in intensity at the bandhead. This intensity anomaly was observed only in emission from the $A^1\Pi (v = 0)$ state. The wavelength positions for the sharp intensity rise of the $A \rightarrow X$ (0, 1), (0, 2), (0, 3), and (0, 4)

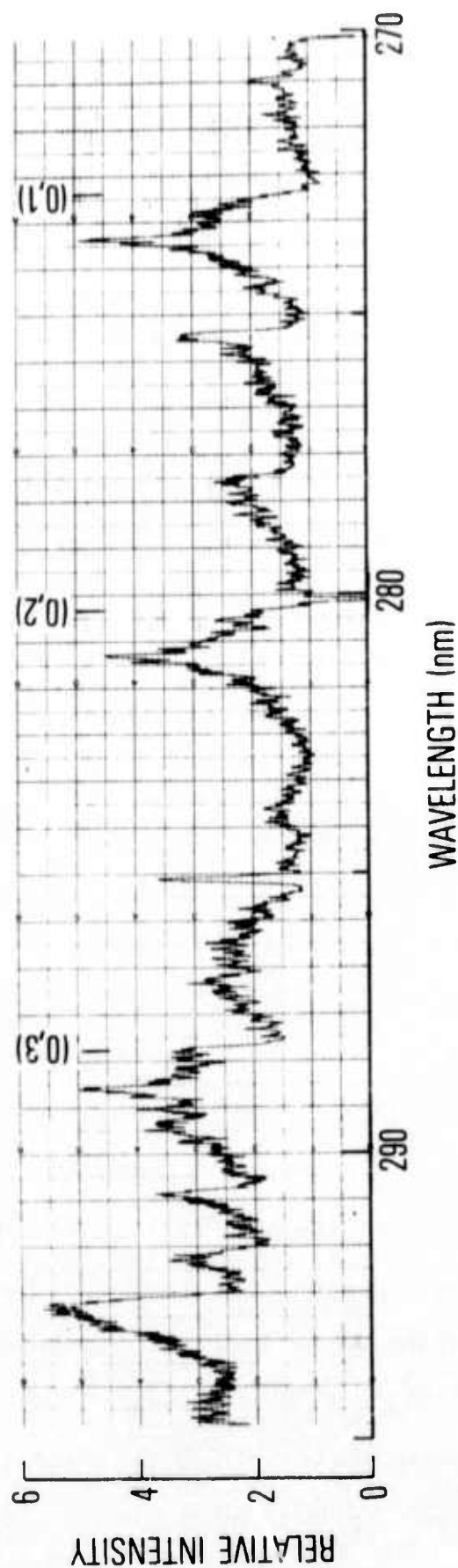


Fig. 4. Spectrum at 0.6 nm resolution of Ge + N₂O flame at a total pressure of 0.6 Torr. The bandheads of the (0, 1), (0, 2), and (0, 3) transitions of A ¹Π → X ¹Σ are labeled. The perturbation in A ¹Π (v = 0) is visible as the more intense peaks roughly 0.8 nm to the red (left) of these bandheads.

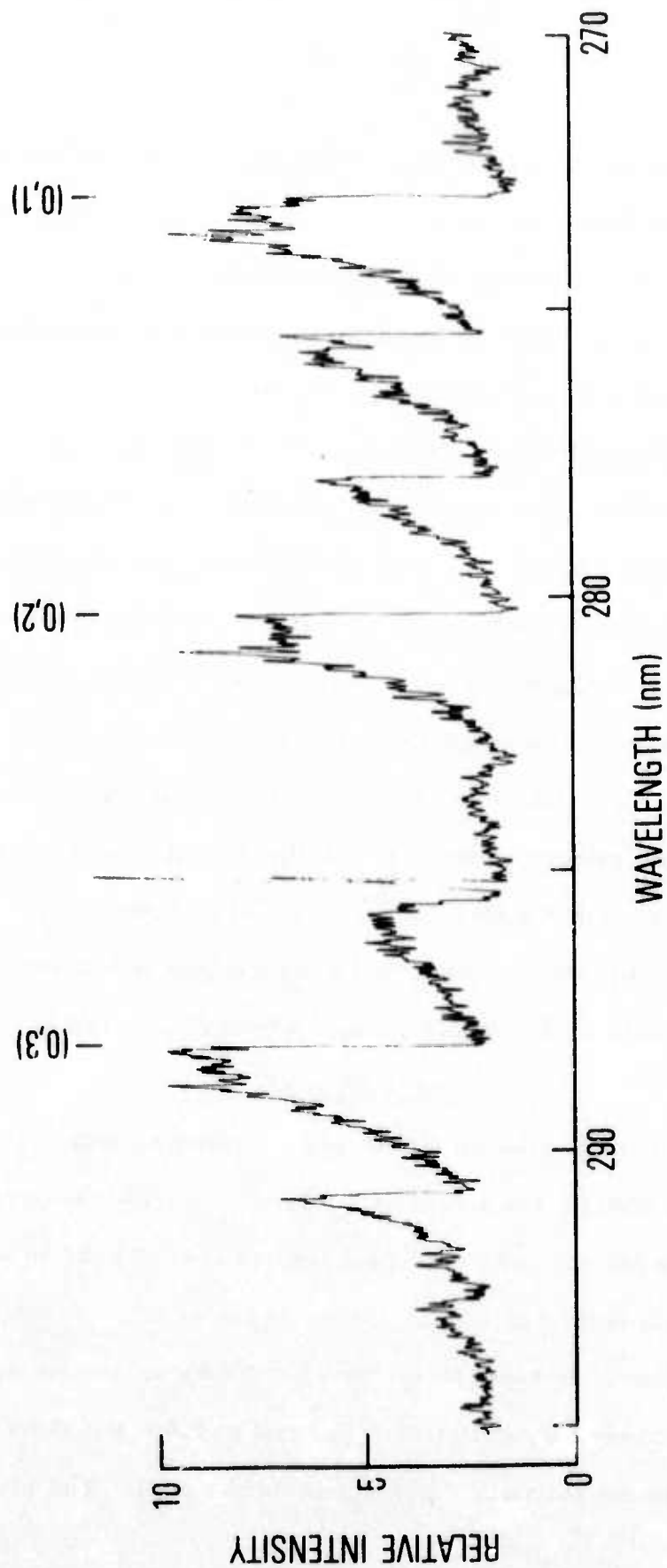


Fig. 5. Spectrum at 0.5 nm. resolution of Ge + N₂O flame at a total pressure of 9.5 Torr. Compare with Fig. 4 and note that now, at higher pressure, the effect of collisions has filled out the $A^1\Pi \rightarrow X^1\Sigma$ (0, 1), (0, 2), and (0, 3) bands, giving them a more normal appearance. The spikes caused by the perturbation are, however, still quite visible in these bands.

bands at low pressures are within 0.05 nm from those expected for the bandheads of the (8,1), (8,2), (8,3), and (8,4) transitions, respectively, of the $b \rightarrow X$ band system. A perturbation between the states A ($v = 0$) and b ($v = 8$), and collisional transfer between these two states, explains the intensity anomalies and their pressure dependence.

C. Chemiluminescent Spectra of the Halide Systems

A green flame was produced from the reaction of Ge vapor with Br_2 in Ar at 0.7 Torr, but because of its very low intensity the emission was not detectable through the monochromator. Hence, no identification was made. The reaction with Cl_2 produced an even weaker flame, too weak to establish the color by eye. Although SF_6 gave no detectable chemiluminescence, the addition of F_2 to Ge vapor gave a purple flame with a weak green fringe. Spectral scans revealed that most of the emission was in the region 368 to 490 nm and was from the GeF ($A^2\Sigma^+ \rightarrow X^2\Pi$) system only.¹¹ The green fringe was probably due to relatively greater amounts of emission from low v' $A^2\Sigma^+$ states at the cooler (outer) edges of the flame.

D. Photon Yields

Absolute photon yield measurements for Ge reacting with N_2O , O_2 , NO , NO_2 , Br_2 , Cl_2 , and F_2 are listed in Table VI. These numbers represent minimum values for the reactive branching ratios. There is little error in the data from the presence of Ge polymeric vapor species since, under the experimental conditions, Ge vaporizes almost entirely as atomic species¹⁹; the probability of a three-body collision involving at least two Ge atoms (which could result in the formation of Ge_2) is very small. The principle

TABLE VI. Photon yields for Ge reacting with various oxidizers.

Oxidizer	Species Produced	Pressure (Torr)	Photon Yield $\times 10^4$					Total
			$A \ ^1\Pi - X \ ^1\Sigma$	$b \ ^3\Pi - X \ ^1\Sigma$	$a \ ^3\Sigma - X \ ^1\Sigma$			
N ₂ O	GeO	0.5	1.0	5.3	6.2			12.5
		10	3.1	5.4	6.8			15.3
O ₂	GeO	0.5	2.2	1.6	0.4			4.2
		10	7.9 ^a	6.2 ^a	7.5 ^a			21.6
NO	GeO	0.5	0.3 ^a	0.2 ^a	-			0.5
NO ₂	GeO	0.5	2.0 ^a	1.9 ^a	1.1 ^a			5.0
Br ₂	-	0.7	$\leq 0.1^b$					
Cl ₂	-	0.7	$\leq 0.1^b$					
F ₂	GeF	0.7	6.8, $A \ ^2\Sigma - X \ ^2\Pi$ system only					

^aThese values are accurate to a factor of 3 only; all others are accurate to a factor of 2.

^bFor any known GeBr or GeCl system between 200 and 500 nm.

source of error in the results, giving an uncertainty of about a factor of 2, was the determination of the Ge weight loss. Variation of the Ge + N₂O photon yields with pressure is consistent with the data shown in Fig. 2.

It can be noted that all of the measured photon yields are very small.

IV. DISCUSSION

The spectroscopic results indicate that the GeO chemiluminescence in the present experiments originates from three different excited electronic states and terminates in the ground electronic state. As is well known for CO,²¹ and as has recently been shown for SiO,²² the lowest-lying molecular states of GeO should also arise from the electron configurations

$$z\sigma^2 y\sigma^2 w\pi^4 x\sigma^2 \quad {}^1\Sigma^+ \quad (2)$$

$$z\sigma^2 y\sigma^2 w\pi^4 x\sigma v\pi \quad {}^1\Pi, {}^3\Pi_r \quad (3)$$

$$z\sigma^2 y\sigma^2 w\pi^3 x\sigma^2 v\pi \quad {}^1\Sigma^-, {}^3\Delta, {}^3\Sigma^+, {}^3\Sigma^-, {}^1\Delta, {}^1\Sigma^+ \quad (4)$$

Configuration (2) gives rise to the X ${}^1\Sigma^+$ ground state, and the A ${}^1\Pi$ state belongs to (3). Molecular states of GeO lower-lying than A ${}^1\Pi$ that can be expected to radiate to the ground state are the ${}^3\Pi_r$ and ${}^3\Sigma^+$ states from (3) and (4), respectively. In CO, the analogous triplet state emissions are the a ${}^3\Pi_r \rightarrow$ X ${}^1\Sigma^+$ Cameron bands and the a' ${}^3\Sigma^+ \rightarrow$ X ${}^1\Sigma^+$ Hopfield-Birge bands. Although for CO the a' ${}^3\Sigma^+$ state is 0.853 eV above²¹ the a ${}^3\Pi_r$ state (comparing T_0 values), recent experimental evidence^{16,17} indicates that for SiO the analogous ${}^3\Sigma^+$ state is 0.055 eV below the ${}^3\Pi_r$ state. Since the a and b states of GeO are the only states lower lying than A ${}^1\Pi$ that are observed in the chemiluminescent spectra, they are identified as the two triplet states expected by analogy with CO and SiO. On the basis of arguments presented below, we assign the a state as ${}^3\Sigma^+$ and the b state as ${}^3\Pi_r$, specifically, ${}^3\Pi_1$.

The ω_e and B_e values of the $^3\Pi_r$ state arising from (3) should be smaller than the ω_e and B_e values of the $X\ ^1\Sigma^+$ ground state since, in the single electron configuration approximation, the $^3\Pi_r$ state has one electron in the strongly antibonding $v\pi$ orbital. In considering the ω_e and B_e values of the $^3\Sigma^+$ state that arise from (4), the magnitudes of these molecular constants should be even smaller than those for the $^3\Pi$ state since the $^3\Sigma^+$ state has only three electrons in the strongly bonding $w\pi$ orbital in addition to one electron in the antibonding $v\pi$ orbital. These qualitative considerations are borne out for the $^3\Pi_r$ and $^3\Sigma^+$ states of CO and SiO, as shown in Table VII. Since the ω_e value of the GeO a state is only 633.3 cm^{-1} compared to the b state value of 734.9 cm^{-1} , the qualitative arguments indicate that the a state is $^3\Sigma^+$ and the b state is $^3\Pi_r$. The assignment of the a $^3\Sigma^+$ state of GeO as lower lying than b $^3\Pi_r$ also presents a monotonic behavior for the ordering of the $^3\Pi$ and $^3\Sigma^+$ states of CO, SiO, and GeO.

Although the Ge isotope splitting is evident in the observed a $^3\Sigma^+ \rightarrow X\ ^1\Sigma^+$ bands, under our experimental resolution the bands appear to be single headed. Assuming Hund's case (b) coupling in the a $^3\Sigma^+$ state, a single head in the R branch is expected for the a $\rightarrow$ X emission. Previous workers^{16,17} have assigned the a state of GeO as $^3\Sigma^+$, partly on the basis of a similar single-headed appearance of the a $\rightarrow$ X bands in their experiments.

Since the spin-orbit coupling constants A for the $(x\sigma)(v\pi)\ ^3\Pi$ states of CO, SiO, and SnO are 41.3 cm^{-1} ,²¹ 73.2 cm^{-1} ,²³ and 560.0 cm^{-1} ,²⁴ respectively, the A value for the b $^3\Pi_r$ state of GeO can be estimated to be

TABLE VII. Comparison of molecular constants of group IVA diatomic oxides.

Molecular State, Constants ^a	CO ^b	SiO ^c	⁷⁴ GeO
X ¹ Σ ⁺			
T ₀	0	0	0
w _e	2 169.8	1 241.4	986.8 ^f
B _e	1.9313	0.7268	0.4857 ^f
a ³ Σ ⁺			
T ₀	55 353.9	33 409 ^d	27 553 ^g
w _e	1 230.7	-	633.3 ^g
B _e	1.3453	-	(0.389) ^h
b ³ Π			
T ₀	48 474.0	33 853 ^d	32 007 ^g
w _e	1743.6	1012 ^e	734.9 ^g
B _e	1.6911	0.6789	(0.438) ^h
A ¹ Π			
T ₀	64 746.5	42 640.4	37 599.4 ⁱ
w _e	1515.6	852.7	650.4 ⁱ
B _e	1.6116	0.6313	0.4133 ^j

^aAll values are given in cm⁻¹.

^bAll of the CO constants are taken from Footnote 21.

^cAll of the SiO constants, except where noted, are taken from Footnote 23.

^dFrom Footnote 17.

^eH. Bredohl, R. Cornet, I. Dubois, and F. Remy, J. Phys. B 7, 666 (1974).

^fFrom Footnote 8.

^gFrom present work.

^hValue is estimated.

ⁱFrom Footnote 3.

^jFrom Footnote 10.

on the order of 150 cm^{-1} . The rotational constant B_e of the $b \ ^3\Pi_r$ state can be estimated from the measured B_e value for the isoconfigurational $A \ ^1\Pi$ state, 0.4133 cm^{-1} ,¹⁰ if a ratio for $B_e(^3\Pi)/B_e(^1\Pi)$ that is similar to that found for CO and SiO is assumed; in this manner, a B_e value of $\sim 0.438 \text{ cm}^{-1}$ is obtained. As the estimated ratio of A/B is 342, we can safely assume that the $b \ ^3\Pi$ state of GeO corresponds to a strong Hund's case (a) coupling limit. Applying well-known selection rules²⁵ to the spin-forbidden $b \ ^3\Pi \rightarrow X \ ^1\Sigma^+$ transition, we find that only the subbands $^3\Pi_{0+} \rightarrow ^1\Sigma^+$, with a P branch and a headed R branch, and $^3\Pi_1 \rightarrow ^1\Sigma^+$, with P and Q branches and a headed R branch, are expected to occur. In the case of the recently observed^{16,17} SiO $b \ ^3\Pi \rightarrow X \ ^1\Sigma^+$ chemiluminescent spectrum, the two expected subbands have been found. Often,¹⁷ the $^3\Pi_1 \rightarrow ^1\Sigma^+$ subband gives the appearance of having two heads, one in the R branch (assuming $B'_e < B''_e$) and one in the Q branch. The Q "head" is not a true bandhead but appears owing to a rapid increase in intensity (from closely spaced Q branch lines) near the band origin. In light of the above discussion, it is surprising, at first, that the GeO bands assigned to the $b \ ^3\Pi_r \rightarrow X \ ^1\Sigma^+$ transition appear to be single headed with no indication of the expected $\sim 150\text{-cm}^{-1}$ spin-orbit splitting. Further considerations indicate the probable reasons for the observed intensity distributions in the GeO $b \ ^3\Pi_r \rightarrow X \ ^1\Sigma^+$ bands.

The observed $b \rightarrow X$ band system of GeO is assigned to the $^3\Pi_1 \rightarrow ^1\Sigma^+$ transition, i. e., $\Omega = 1 \rightarrow \Omega = 0^+$. Assuming that the Q branch heads of this transition are close to the band origins, the energy separation between the R and Q branch heads is given approximately by²⁶

$$\Delta\nu = \frac{-(B_{v'} + B_{v''})^2}{4(B_{v'} - B_{v''})} \quad (5)$$

Substitution of the measured value $B_e'' = 0.486 \text{ cm}^{-1}$ and the estimated value $B_e' = 0.438 \text{ cm}^{-1}$ into (5) yields $\Delta\nu = 4.4 \text{ cm}^{-1}$. As the $b \rightarrow X$ bands have been observed under only $\sim 5\text{-cm}^{-1}$ resolution in the present study, the single-headed appearances of the $b^3\Pi_1 \rightarrow X^1\Sigma^+$ bands are not unexpected.

Emission from $b^3\Pi_{0+}$, expected $\sim 150 \text{ cm}^{-1}$ to the red of the $b^3\Pi_1 \rightarrow X^1\Sigma^+$ bandheads, has not been observed. The intensity of the $b \rightarrow X$ forbidden transitions most likely arises from spin-orbit mixing of the $b^3\Pi_r$ state with the $A^1\Pi$ state, that is, we can neglect any mixing of $b^3\Pi_r$ with $^1\Sigma$ states. In the Hund's case (a) limit, the spin-orbit interaction mixes $A^1\Pi_1$ with only the $^3\Pi_1$ substate of $b^3\Pi_r$.^{27,28} Thus, at low J values, only the $b^3\Pi_1 \rightarrow X^1\Sigma^+$ subband is expected to be observable. As J increases, the $^3\Pi_0$, $^3\Pi_1$, and $^3\Pi_2$ substates become mixed owing to spin uncoupling and a gradual transition towards Hund's case (b) coupling. The mixing of $^3\Pi_0$, $^3\Pi_1$, and $^3\Pi_2$ is then a function of J , and as J increases, the $b^3\Pi_{0+} \rightarrow X^1\Sigma^+$ subband should acquire intensity. For $1 < J < A/(2)^{1/2} B$, the amount of $^3\Pi_1$ character mixed into $^3\Pi_{0+}$ is approximately $2B^2J^2/A^2$.²⁹ Now A/B for the $b^3\Pi$ state of GeO is about three times that for SiO, thus, emission from GeO $b^3\Pi_{0+}$ will acquire intensity at J values roughly three times those where SiO $b^3\Pi_{0+}$ emission begins. It seems likely that GeO $b^3\Pi_{0+} \rightarrow X^1\Sigma^+$ bands acquire intensity only at J values well away from those J values where the

bandheads form; this would explain why emission from $b^3\Pi_{0+}$ has not been observed.

Rydberg-Klein-Rees potential energy curves have been calculated³⁰ for the $\text{GeO } X^1\Sigma^+$, $a^3\Sigma^+$, $b^3\Pi_r$, and $A^1\Pi$ states with the molecular constants given in Table VII. It was necessary to estimate the rotational constants for the two triplet states. The estimation of $B_e(b^3\Pi_r)$ was described above; $B_e(a^3\Sigma^+)$ was estimated using the relation³¹ $B_e = \omega_e/1626$, where 1626 is the average value of ω_e/B_e for the $A^1\Pi$ and $b^3\Pi_r$ states. The RKR potential functions were then used to calculate³⁰ Franck-Condon factors, given by $q_{v',v''} = |\langle v' | v'' \rangle|^2$, for the three observed GeO band systems. The Franck-Condon factors are tabulated in Tables I, II, and IV for the $A^1\Pi \rightarrow X^1\Sigma^+$, $b^3\Pi_1 \rightarrow X^1\Sigma^+$, and $a^3\Sigma^+ \rightarrow X^1\Sigma^+$ transitions, respectively. Although use of the calculated Franck-Condon factors to predict relative band intensities for the two intercombination systems has to be less reliable because of the use of estimated molecular constants and the neglect of triplet state mixing with the $A^1\Pi$ state,²⁸ the values obtained correlate with the observed relative band intensities remarkably well. In just about every case where a very low Franck-Condon factor for a particular transition has been calculated, for example the $A-X(1,3)$, $b-X(1,1)$, and $a-X(0,0)$ bands, the band corresponding to that particular transition is missing in the chemiluminescent spectrum. The calculated Franck-Condon factors tend to support the present interpretation of the GeO spectra and the molecular constants obtained from the spectra.

The Franck-Condon factors calculated for the $b \rightarrow X$ (8,1), (8,2), and (8,3) transitions are small (see Table II), yet bands of appreciable intensity are observed near the calculated wavelengths for these transitions at low pressures. The $b \ ^3\Pi_1$ ($v = 8$) state should be quite metastable since the mixing with the nearby $A \ ^1\Pi$ ($v = 0$) state will be small on account of the low $\langle \ ^3\Pi_{v=8} | \ ^1\Pi_{v=0} \rangle$ vibrational overlap. It seems more likely that the intense features observed are due to perturbed $A \ ^1\Pi$ ($v = 0$) rotational levels as stated in the results. Stating the effect in a nonmathematical manner, the $b \ ^3\Pi$ ($v = 8$) population will build up because of the metastability, wherein these molecules escape by an intersystem crossing to the $A \ ^1\Pi$ ($v = 0$) state and then radiatively relax to the ground state.

In support of spin correlation arguments for the reaction of ground state Ge atoms with N_2O , Fig. 2 could be interpreted as showing that a triplet state ($b \ ^3\Pi$) is initially formed preferentially; only with increasing numbers of collisions, brought about by increasing the pressure, does the relative intensity of emission from $A \ ^1\Pi$ increase, which suggests the importance of secondary collisions informing the singlet A state.

If we compare our results to previous work, it is clear that we have observed the same $GeO \ a \ ^3\Sigma^+ \rightarrow X \ ^1\Sigma^+$ system as Hadley and co-workers^{16,17} found in the Ge (from GeH_4) + N_2O chemiluminescent spectrum. These authors failed to observe the $b \ ^3\Pi_1 \rightarrow X \ ^1\Sigma^+$ and $A \ ^1\Pi \rightarrow X \ ^1\Sigma^+$ systems, which are quite intense in our spectra, probably because of their use of He as a carrier gas (see above, results of changing carrier) coupled with the weakness of the emission they saw, and perhaps also because of quenching from the

products of the GeH_4 discharge. Many of the GeO bands we have assigned to $b\ ^3\Pi_1 \rightarrow X\ ^1\Sigma^+$ were observed previously in the $\text{O} + \text{GeH}_4$ chemiluminescent study¹² where they were left unassigned or were assigned, incorrectly, to $A \rightarrow X$ emissions. Finally, the analysis of the thermal emission spectrum of GeO from the reaction of Ge vapor with air¹⁵ would seem to be in error.

FOOTNOTES

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