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Chemiluminescence Spectra and Photon Yields for Several Sn-Oxidizer Reactions

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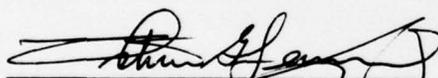
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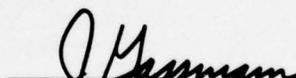
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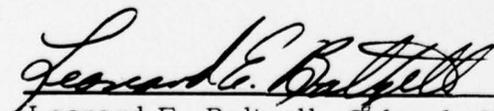
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Tin vapor has been reacted with N ₂ O, NO ₂ , O ₂ , and F ₂ to produce SnO and SnF in a flame. Reactions of Sn with O ₂ and NO ₂ produced very weak chemiluminescence, whereas Sn + Br ₂ and Cl ₂ produced no detectable light emission. The highest photon yield measured was 6.7% for SnO emission that resulted from the reaction of Sn + N ₂ O in Ar at a Sn concentration of 3 x 10 ¹³ /cm ³ . The maximum SnF yield measured was 0.3% for Sn + F ₂ . The spectral character of the SnO chemiluminescence generated in the Sn + N ₂ O reaction was found to be a strong function of pressure (0.5 to 25 Torr)		

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and carrier gas identity (Ar, He, N₂) in the flow-tube reaction system. ←
Extension of the SnO a-X system yielded the following constants (all in
cm⁻¹):

$$a^3\Sigma^+(1): \quad T_e = 20622.6 \pm 2.5, \quad \omega_e = 554.0 \pm 1.7, \quad \omega_e x_e = 2.45 \pm 0.36$$

and

$$X^1\Sigma: \quad \omega_e = 823.40 \pm 0.99, \quad \omega_e x_e = 3.77 \pm 0.10$$

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PREFACE

The authors thank R. Steele for his assistance with the pulsed lasers, and Dr. H. P. Broida for his hospitality. The work of C. Linton was supported by the Air Force Office of Scientific Research under Grant No. AFOSR-74-2724. His present address is: Physics Department, University of New Brunswick, Fredericton, New Brunswick, Canada.

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I. INTRODUCTION

Diatomic group IVa (Carbon group) oxides, halides, nitrides, and hydrides have been predicted¹ to be good chemical laser candidate systems. Tin oxide is particularly significant because photon yields as high as 50% have been measured for the $\text{Sn} + \text{N}_2\text{O}$ reaction.² In the experiments described here, tin vapor was reacted with N_2O , NO_2 , O_2 , Br_2 , Cl_2 , and F_2 in a flow system, and the chemiluminescent flames, if any, were measured for spectral character and absolute photon output, as a function of pressure and carrier gas, which permitted calculation of photon yields when the Sn flow rate was known. The SnO flame was irradiated by the output of several lasers (Ar^+ , cw dye, pulsed dye, and N_2), but only the N_2 laser (337.1 nm) produced detectable photoluminescence, for which a radiative lifetime was measured.

II. EXPERIMENT

Sn vapor was produced by the heating of Sn metal to temperatures near 1600 K (as measured with an optical pyrometer); the vapor was entrained in an Ar carrier gas flow, and the near-room-temperature mixture was reacted with numerous gases in a previously described flow system.³ The Sn flow rates were 0.25 to 2.0×10^{17} atoms/sec, whereas those for Ar, the carrier gas normally used, were 1.0 to 2.2×10^{21} atoms/sec, or about four orders of magnitude greater than the Sn flow rates. The Sn vapor is assumed to be primarily monatomic.⁴ Thus, the concentration of Sn vapor that initially enters the reaction zone at 10 Torr total pressure is approximately 3.5×10^{13} atoms/cm³, and its flow velocity is calculated to be 1.2 to 5×10^3 cm/sec.

Spectra were recorded photoelectrically by using a 1 m Czerny-Turner spectrometer with various photomultiplier and grating combinations. Photon yield measurements were made on oxidant-rich flames by a method described previously.⁵ Photoluminescence measurements were made by directing a laser (2 W Ar⁺, 200 mW cw dye, 2 kW pulsed dye, and 200 kW N₂) horizontally through the Sn + O₂ flame and observing at right angles to both the laser beam and the flame axis with a photomultiplier or by visual observation.

III. RESULTS AND DISCUSSION

A. $\text{Sn} + \text{N}_2\text{O}$

The addition of N_2O to a stream of $\text{Sn} + \text{Ar}$ resulted in a bright flame that was closed at pressures above 7 Torr but open, i. e., the chemiluminescent column extended beyond the observation limits defined by the windows of the flow system, at 5 Torr and below. This was probably caused by the relatively slow $\text{Sn} + \text{N}_2\text{O}$ reaction rate² rather than the long SnO radiative lifetime.⁶ To the eye, the flame at 10 Torr appeared blue with a green sheath. Its spectrum, which we measured from 220 to 800 nm, contained the $a^3\Sigma^+(1)$, $b^3\Pi(O^+)$, $b'(1)$, and $A^1\Pi \rightarrow X^1\Sigma^+$ systems of SnO (see below for discussion of systems) and was similar to that observed by other experimenters.^{2,7} The spectral composition of the $\text{Sn} + \text{N}_2\text{O}$ flame, and its visual appearance, changed significantly with changes in the total system pressure and carrier gas identity. In Ar, as the pressure was increased from 0.5 to 25 Torr, the flame changed from a diffuse blue column that extended out of sight toward the pump to a low, compact, cone-shaped blue flame fringed in green. In He, as the pressure increased from 0.5 to 25 Torr, the flame developed from a diffuse blue center surrounded by a yellow-green glow that filled the reaction vessel to a closed, elongated, diffuse sphere that was blue on the bottom and yellow green above. With N_2 as the carrier gas, the appearance and pressure behavior were similar to those with Ar, except that the low-pressure blue column was sheathed in green, and at higher pressures, there was relatively more green. In Fig. 1, the spectra of $\text{Sn} + \text{N}_2\text{O}$ flames are compared under these varying conditions of pressure and carrier gas. As the pressure increased, the intensity of the long-wavelength end of the spectrum increased relative to the short-wavelength end. Closer examination revealed that, over the entire pressure range covered, it was primarily the a system that increased relative to the other systems (Fig. 2).

In order to determine how the populations of the various electronic and vibrational states vary with conditions, the same intensity ratio method was

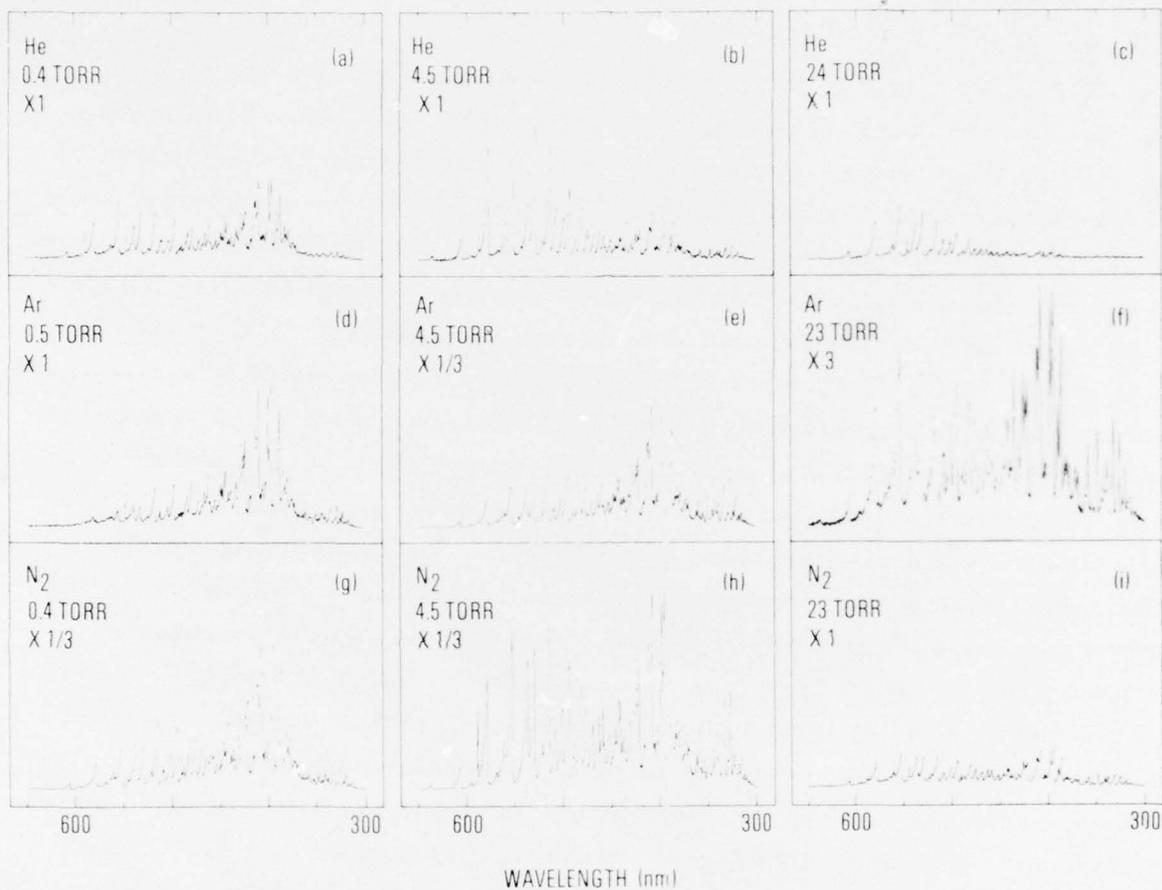


Figure 1. Comparison of Sn + N₂O Chemiluminescence Between 300 and 650 nm for He, Ar, and N₂ Carriers at Various Pressures. The Spectra should be compared relatively, not absolutely, because changes in carrier gas and pressure also affect the absolute intensity by causing changes in the metal flow rate. Spectra are uncorrected for instrument response. Note the increase of a-X emission at higher pressure.

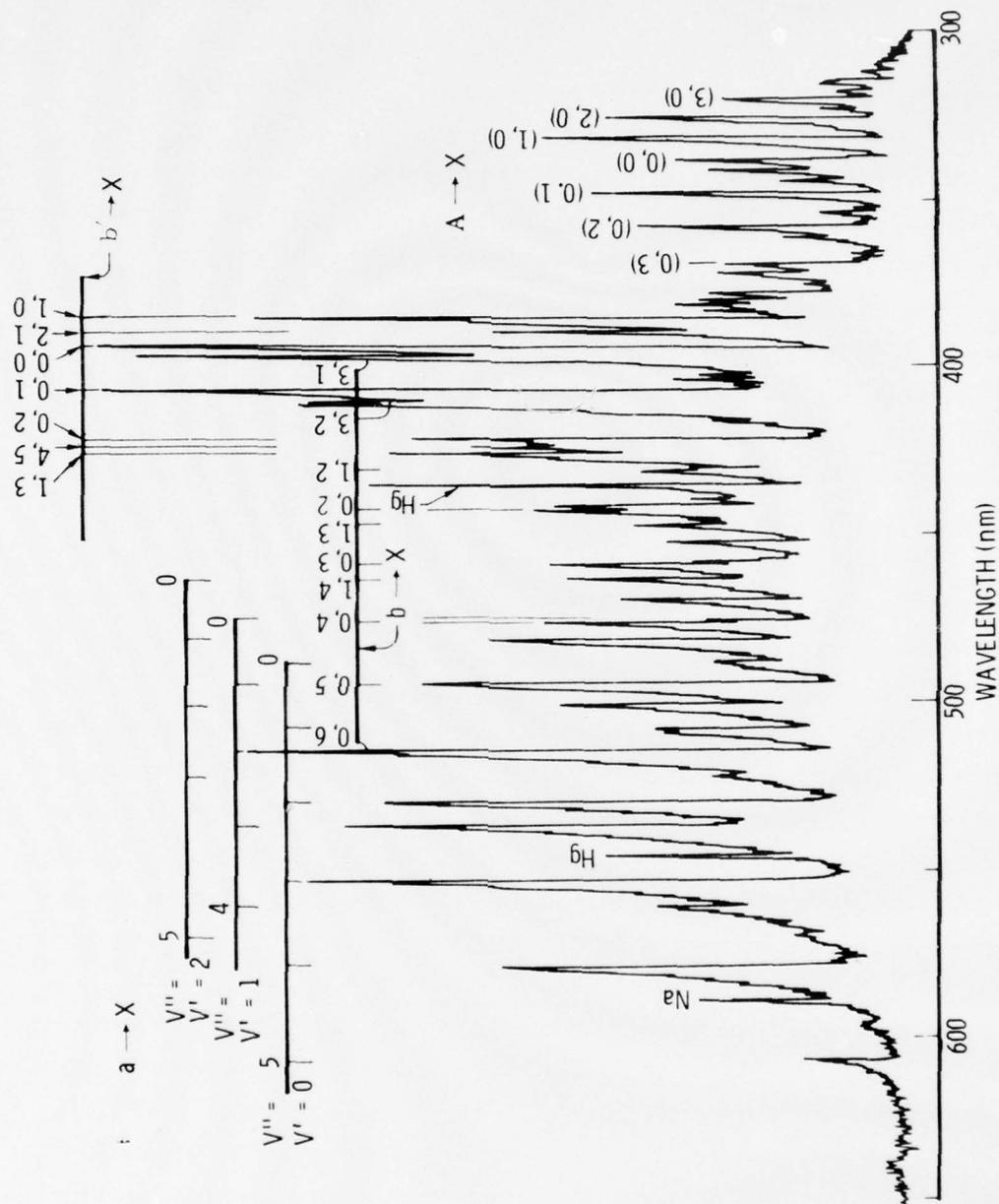


Figure 2. Detail and Labeling Key for Figure 1. This is an enlargement of Figure 1f.

used as for PbO.⁸ Briefly, the ratio $R = I_1/I_2$ of the intensities of a given band under two sets of conditions, 1 and 2, is independent of probability parameters and instrument and detector response characteristics. A plot of $\log R$ for various bands of each band system versus the energy of the upper state of the band will be linear if the electronic and vibrational populations change from one Boltzmann distribution to another. In Fig. 3, it is clear that the plots are not linear, and that a Boltzmann description of the electronic state populations is not valid. However, the individual plots for the vibrational levels of the a and A states are linear, which shows that vibrational relaxation of these states follows a Boltzmann mechanism, and that the vibrational temperature decreases as the pressure increases. At lower pressures (Fig. 3a) both states behave in a similar manner, and at higher pressures (Fig. 3b), the a-state emission increases relative to that of the A $^1\Pi$ state. The b $^3\Pi(O^+)$ and b'(1) states behave in a similar manner. They both decrease in population relative to the a state as the pressure increases. At lower pressures (≤ 5 Torr), they also decrease in population relative to the A $^1\Pi$ state (Fig. 3b). The variation among the vibrational levels of these states was not large enough to detect any definite trends within the accuracy of the measurements. It was observed in Pb + N₂O flames⁸ that the temperature in the crucible decreased as the carrier gas was changed from Ar to N₂ to He. The intensities of the SnO bands are very sensitive to temperature changes in the crucible, and it is likely that the observed variations with carrier gas can be explained, at least partly, as a temperature effect.

B. Sn + O₂

Sn + O₂ in Ar, which, on energy considerations, is predicted to form only ground state SnO,⁹ produced a closed, well-defined, but very weak, blue-purple flame that was quite sensitive to O₂ flow. Slightly more or less than the optimum amount of O₂ caused the flame to disappear, and the optimum O₂ flow rate was much less than the optimum, i.e., for brightest chemiluminescence, N₂O flow rate. This indicates that O₂ might be not only a poor producer of electronically excited SnO, but also a good quencher of it. The addition

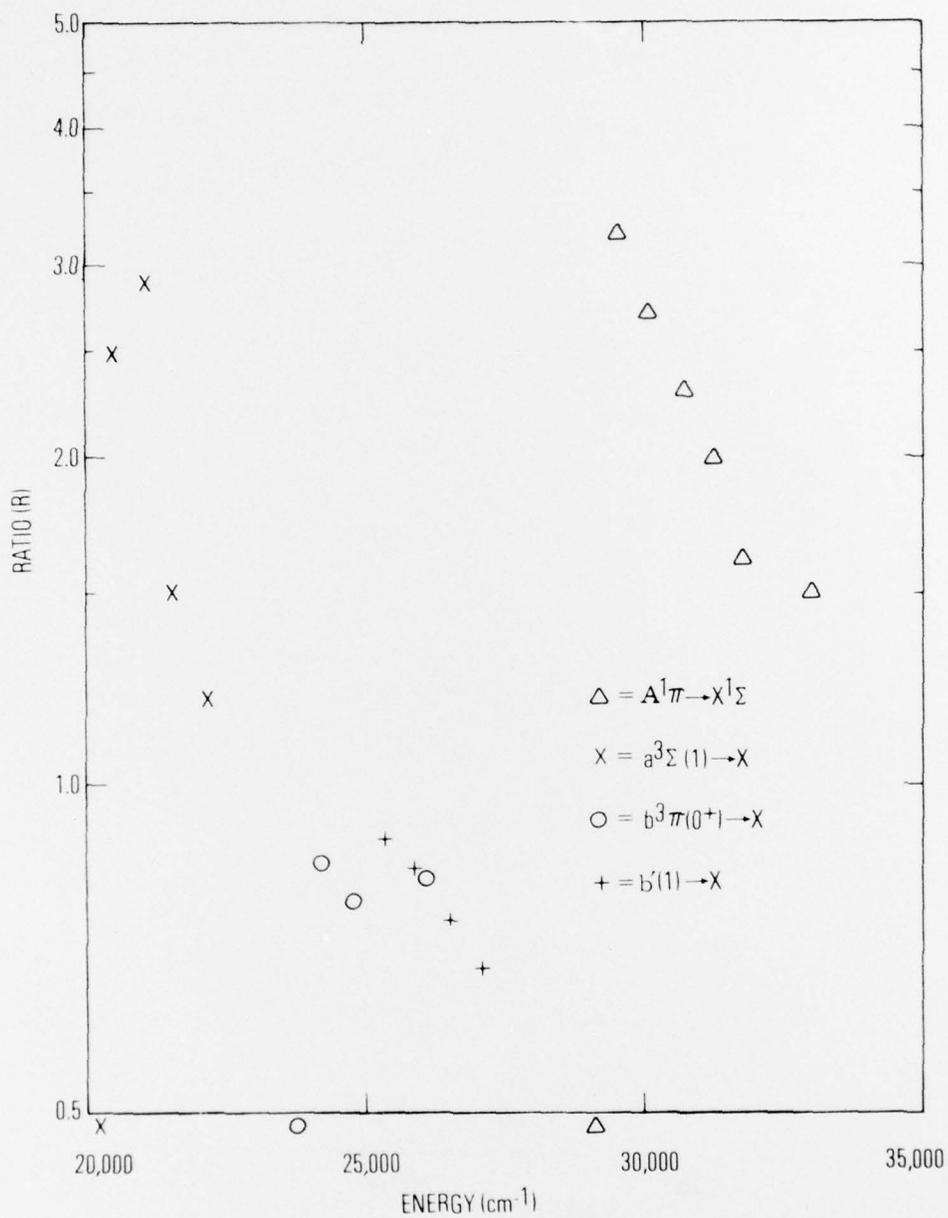


Figure 3a. Plot of Log R, the Ratio of Intensities of a Given Band at Two Different Argon Pressures, vs the Energy of the Upper State of the Band for a Sn + N₂O Flame. $R = I(5 \text{ Torr})/I(1 \text{ Torr})$. The uncertainty in the ratio is about 30%.

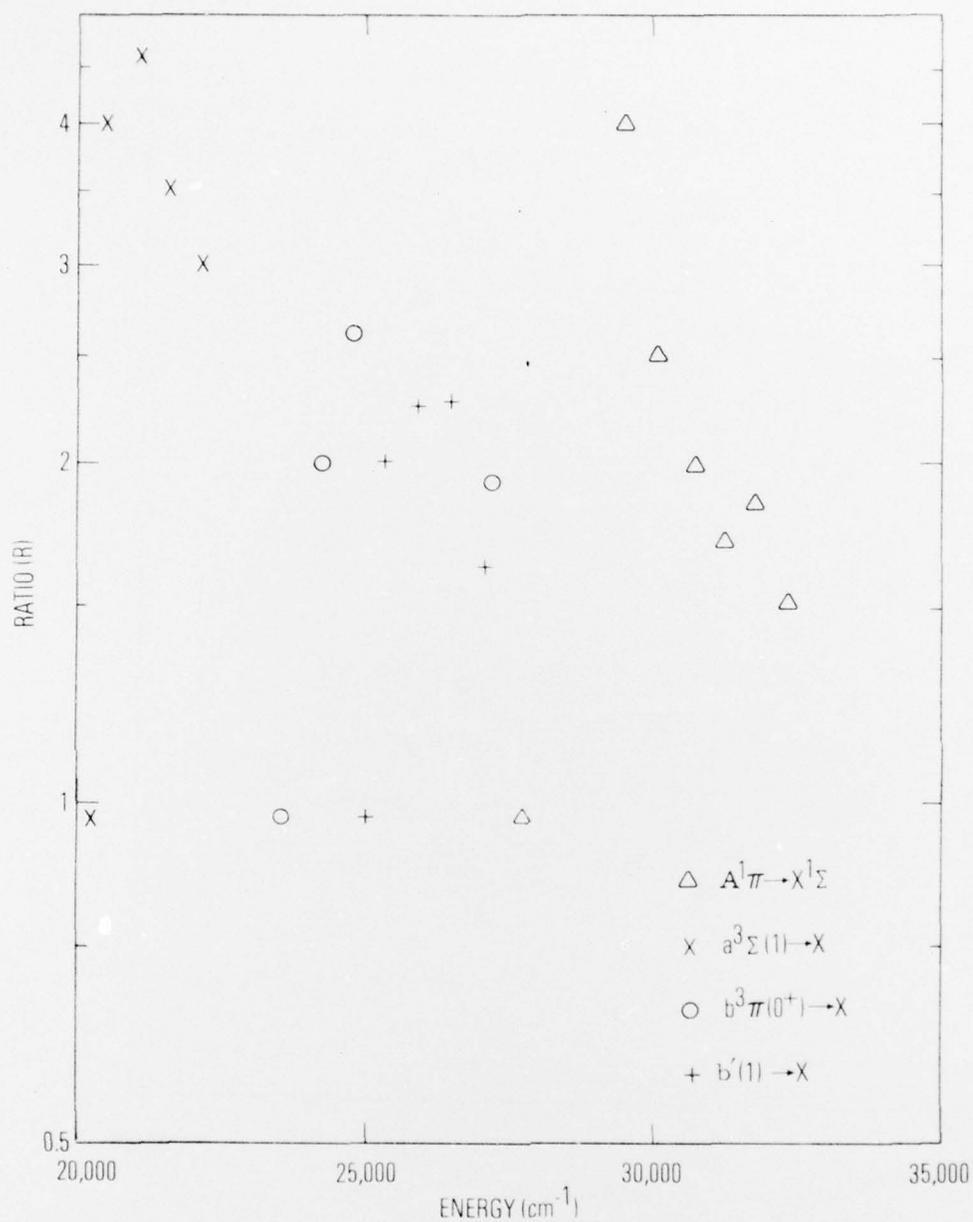


Figure 3b. Plot of Log R, the Ratio of Intensities of a Given Band at Two Different Argon Pressures, vs the Energy of the Upper State of the Band for a Sn + N₂O Flame. R = I(24 Torr)/I(5 Torr). The uncertainty in the ratio is about 30%.

of a small flow of O_2 , by means of a ring-shaped injector, near the bottom of a $Sn + N_2O$ flame caused a large decrease in the SnO light emission. This was caused either by the competition of the dark $Sn + O_2$ reaction for Sn atoms or by the O_2 quenching of excited SnO , or both. NO_2 in Ar produced a similar weak-to-invisible flame.

C. SPECTROSCOPY OF SnO

There appears to be some confusion in the literature about the lowest excited states of SnO , all of which have been identified through band systems connecting them with the ground state. In Rosen's tables,¹⁰ the lowest excited states are listed as A and B and have been suggested¹¹ to be the $\Omega=0^+$ and 1 components of a $^3\Pi$ state, most probably equivalent to a $^3\Pi$ of CO and to $b^3\Pi$ of SiO and GeO . Joshi and Yamdagni (JY)¹² divided the complete spectrum above 350 nm into four systems: A, B, C, and D-X. On closer examination, it appears that their B and C systems correspond, with some changes in vibrational assignments, to Rosen's A and B systems. The A-X system was new, and the D-X system remained unaltered from previous tabulations. Recently, Linevsky and Carabetta (LC)⁷ extended the spectrum to 750 nm and, on the basis of their new measurements, reassigned most of JY's A system, together with many new bands, to a new system, which they labeled a $^3\Sigma^+ - X^1\Sigma^+$. This state is the lowest observed excited state of SnO , and its energy has been shown to fit very well into the trend of the lowest observed $^3\Sigma^+$ states of the other group IVA oxides.¹³ The appearance of the spectrum is very similar to that of the a, A, B, and D-X systems of PbO . In maintaining as much consistency as possible with both the labeling of the other group IVA monoxides (CO ,¹⁰ SiO ,¹⁴ GeO ,⁵ and PbO ¹³), we use the following labeling for the lowest excited states of SnO :

$$\begin{aligned}
 a^3\Sigma^+(1), & \quad T_{oo} = 20900 \text{ cm}^{-1}; \\
 b^3\Pi(0^+), & \quad T_{oo} = 24199 \text{ cm}^{-1}; \\
 b'(1), & \quad T_{oo} = 25318 \text{ cm}^{-1}; \text{ and} \\
 A^1\Pi, & \quad T_{oo} = 29505 \text{ cm}^{-1}.
 \end{aligned}$$

The electronic states of CO, SiO, and GeO are described by coupling cases (a) and (b) and the PbO states by case (c). As the exact nature of the coupling in SnO has not yet been determined and is probably intermediate between the two extremes above, the a and b states are written in mixed notation. The $b^3\Pi(0^+)$ and $b'(1)$ states (JY's B and C states), which are known to be 0^+ and 1 symmetry,¹¹ appear to be analogous to the $A(0^+)$ and $B(1)$ states of PbO.⁸ See correlation diagram of Oldenberg et al.¹³ $b'(1)$ has not been labeled $b^3\Pi$ because recent data^{7,15} suggests that $b'(1)$ is possibly not the $\Omega = 1$ component of the lowest lying $^3\Pi$ state. Under our experimental conditions, however, a similarity was observed in the behavior of the $b^3\Pi(0^+)$ and $b'(1)$ states with changing conditions. The correctness of the LC analysis⁷ was confirmed in the present experiments by using spectra from which wavelengths were measured to an accuracy of 0.05 nm. Several new fairly intense bands served to extend the analysis of the $a^3\Sigma(1) - X$ system and extended observations of the a state to higher vibrational levels. The variation of the intensities of the bands with pressure and carrier gas further confirmed the assignment of these bands. The new bands are listed in Table I, and the vibrational constants (in cm^{-1}) calculated from a least-squares fit to all the known bands of the system are

$$a^3\Sigma(1): \quad T_e = 20622.6 \pm 2.5, \quad \omega_e = 554.0 \pm 1.7, \quad \omega_e x_e = 2.45 \pm 0.36$$

and

$$X^1\Sigma: \quad \omega_e = 823.40 \pm 0.99, \quad \omega_e x_e = 3.77 \pm 0.10.$$

Several bands showed clear isotopic heads for Sn^{118} and Sn^{120} , and the separation of these heads is consistent with the vibrational assignments.

D. Sn + HALOGENS

The reaction of Sn with Br_2 and Cl_2 produced no detectable chemiluminescence. $\text{Sn} + \text{F}_2$ in Ar, which is about 2.3 eV exothermic for the formation of SnF ,⁹ produced a bright, short, compact, turquoise-blue flame. The flame was closed even at 1 Torr, which indicates a shorter lifetime or a much

Table I. New bands of the $a^3\Sigma^+(1) - X^1\Sigma^+$ system of SnO

v'	v''	Wavelength, nm	Wavenumber, cm^{-1}	
			Observed	Obs. - Calc.
5	0	4312.3	23183.0	-1.8
4	0	4412.5	22656.5	1.3
3	0	4518.5	22125.0	4.2
4	1	4577.5	21839.9	0.5
2	0	4632.6	21580.1	-1.4
3	1	4692.1 ^a	21306.5	1.5
1	0	4752.5	21035.7	-1.6
2	1	4814.5 ^a	20764.8	-0.9
1	1	4943.8	20221.7	0.3
3	4	5288.5	18903.7	1.2
3	5	5517.9	18117.8	1.0
1	6	6149.8	16256.2	1.2

^aAlso observed by Linevsky and Carabetta.⁷

faster reaction rate, or both, than for $\text{Sn} + \text{N}_2\text{O}$. The emission came primarily from two spectral regions: (1) 600 to 415 nm, which was $\text{SnF} (\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi_{3/2} \text{ and } 1/2)$, and (2) 400 to 310 nm, a broad, banded system that does not correspond to any known SnF system (Fig. 4); the strongest bands of this system are at 364.9, 362.7, 359.9, 357.5, and 354.9 nm (± 0.5 nm). A broad, very weak emission feature, for which no structure could be detected, was observed between 240 and 280 nm, which could correspond to $\text{SnF} \text{ C, D, or E} \rightarrow \text{X}^2\Pi$. Very weak emission was also observed in the 280 to 320 nm range, which was identified as $\text{SnF} (\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Pi_{1/2})$ [primarily (0, 0), (0, 1), and (0, 2)]; some $\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Pi_{3/2}$ bands also appear to be present in the same region. The $\text{B}^2\Sigma$ state lies at about 4 eV, which is considerably more than the $\text{Sn} + \text{F}_2$ reaction exothermicity, above the ground state.

E. PHOTON YIELDS

Photon yields measured for the above reactions are listed in Table II. $\text{Sn} + \text{N}_2\text{O}$ and $\text{Sn} + \text{F}_2$ are the only reaction systems that appear to be of possible interest as chemically pumped laser systems. The maximum $\text{Sn} + \text{N}_2\text{O}$ photon yield of 6.7% measured here (for all photons in the range 220-800 nm) is considerably larger than the LC measurement⁷ of 1 to 2%, but their result is a lower bound, and thus the numbers are not in disagreement. The 6.7% is, however, much less than the 31 to 53% values given by Felder and Fontijn² for $\text{Sn} + \text{N}_2\text{O}$ in Ar at 10 Torr. The apparent disagreement is large, even when considering the factor of two accuracy cited for their work and for the present work. There were significant differences, however, in the experimental methods used both for photon calibration and for tin flux measurements. Also, their tin atom concentrations in the reaction zone ($2 \times 10^{11}/\text{cc}$) were about two orders of magnitude lower than those used here. It is possible that Sn could be a quencher of electronically excited SnO. This effect is already known for the $\text{Ba} + \text{N}_2\text{O}$ system.¹⁶ It is also possible that, at the higher concentrations in our flame, Sn atoms begin to dimerize, which prevents the efficient formation of SnO because the Sn_2 bond energy is 2 eV.⁹ Finally, and perhaps most importantly, our flame operated with reactants that were

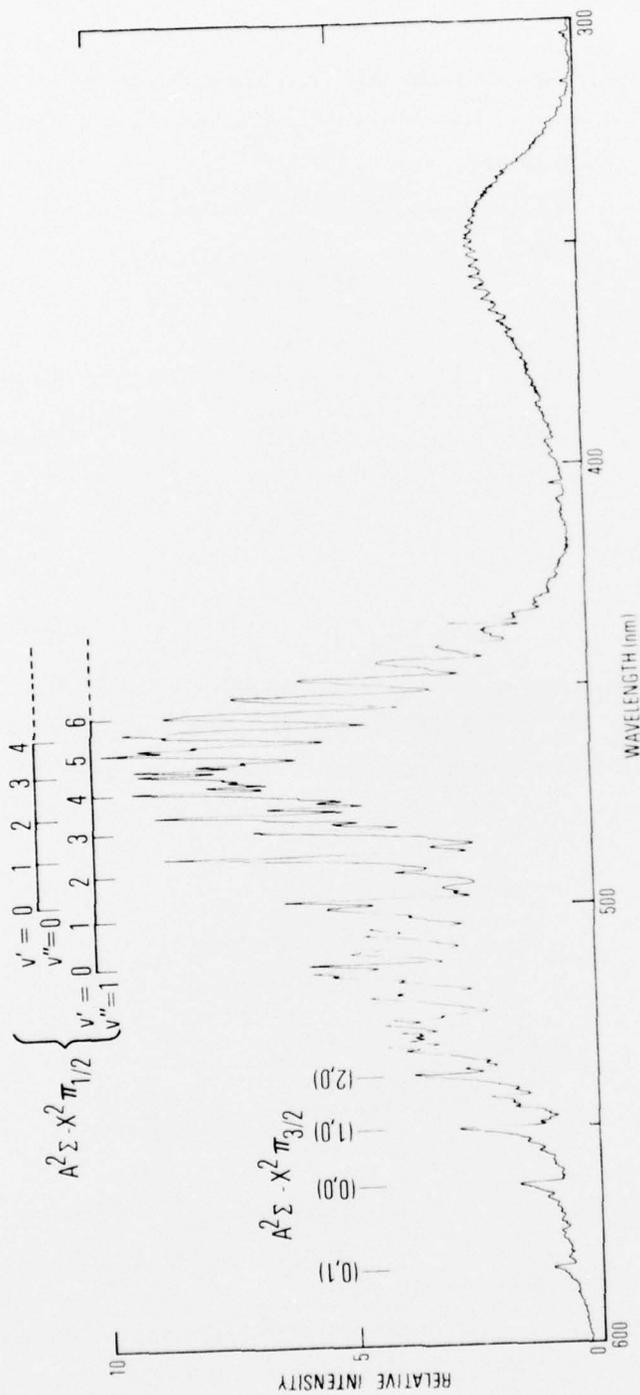


Figure 4. Spectrum of Sn + F₂ Flame in Ar at 5 Torr. The Hg lines at 435.8 and 404.7 nm are from the room lights.

Table II. Measured photon yields for Sn reactions in Ar

Oxidizer	Pressure, Torr	Emitting Species	Sn Flow, atoms $\times 10^{17}$ /sec	Measured Yield, %
N ₂ O	5.2	SnO	1.24	4.1
	9.5		0.25	6.7
	20		0.95	5.1
O ₂	5.2	SnO	1.24	0.08
F ₂	5.4	SnF	1.24	0.26 ^a
	9.5		0.94	0.22 ^a
	20		0.95	0.31 ^a
Br ₂	5			<0.01
Cl ₂	5			<0.01

^a90 to 95% of this yield was from SnF ($A^2\Sigma - X^2\Pi$), and most of the remainder was from the 310 to 400 nm system, which could not be identified.

just slightly above room temperature, whereas Felder and Fontijn's experiments were carried out with the reactants at elevated temperatures. They have, in fact, measured a significant temperature dependence of the photon yield for $\text{Sn} + \text{N}_2\text{O} \rightarrow \text{SnO}$.¹⁷ We found that, under conditions of excess metal, i.e., with a small measured flow of N_2O , increasing the crucible temperature from 1575 to 1635 K (which also increases the temperature of the Ar-Sn mixture) nearly doubles SnO A-X and b'-X emission intensity, increases b-X emission by about a factor of 1.5, and has very little effect on the a-X system. Furthermore, in the normal (excess N_2O) operating condition, increasing the crucible temperature, which necessarily also increases the tin evaporation rate, not only increases the light output, but also shortens the flame, which implies an increased reaction rate constant.

F. PHOTOLUMINESCENCE

With the use of several lasers, efforts were made to stimulate photoluminescence in the $\text{Sn} + \text{O}_2$ flame at 2 Torr. The Ar^+ laser (2 W total, each line between 528.7 nm and 454.5 nm individually prism selectable), cw dye laser (200 mW max, $\lambda = 640$ to 570 nm and 560 to 520 nm, continuously tunable), and N_2 -laser-pumped dye laser (1 to 2 kW, $\lambda = 640$ to 570 nm, 491 to 445 nm, and 425 to 415 nm) all failed to produce any detectable SnO photoluminescence. The only detectable signals were the sodium D lines near 589 nm. This indicates either that there is very little ground-state SnO available to absorb a photon or that the transition probabilities of the a, b, and b'-X systems are small. The nitrogen laser (10 nsec, 200 kW, 337.1 nm) did produce a detectable signal with a measurable lifetime. Because the N_2 laser is not tunable and the photoluminescence was not strong enough to permit spectral analysis, it was not possible to determine absolutely the emitter's identity. However, because the signal disappeared when either the Sn or O_2 flow was turned off, and because it maximized at an O_2 flow that gave a compact blue flame, it is probable that SnO was excited, as there was no evidence for the presence in the flame of molecules other than SnO and O_2 . The only known SnO system that the N_2 laser could have excited is $\text{A}^1\Pi \leftarrow \text{X}^1\Sigma^+$, and the short lifetime

that was measured is indicative of such an allowed transition. Decay measurements taken at 9.7, 4.8, and 0.85 Torr total pressure (Fig. 5) actually revealed two decay times: one with a moderate pressure dependence that extrapolated to 160 ± 20 nsec at zero pressure, and one with a very strong pressure dependence that extrapolated to 130 ± 60 nsec. These short zero pressure decay times make SnO ($A^1\Pi - X^1\Sigma$) unattractive as a cw laser system, unlike the a, b, and b' - $X^1\Sigma$ systems. The a, b, and b' states, which correlate with the low-lying triplet states of other group IVA monoxides, are expected to have fairly long radiative lifetimes. In view of the reasonably large photon yields, these states appear to be promising chemical laser candidates, particularly when it is remembered that the measured photon yields represent a lower limit to the actual reaction branching ratio.

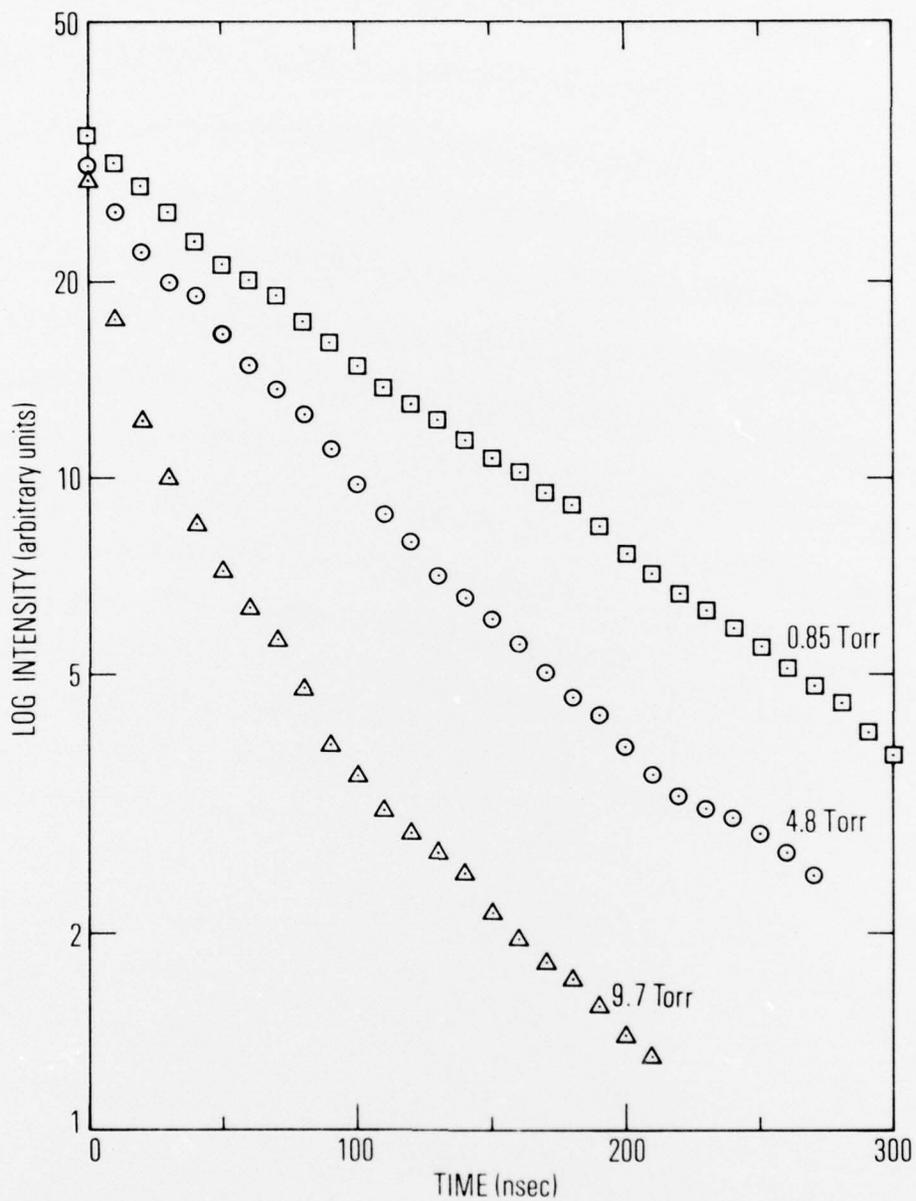


Figure 5. Plot of Log Intensity of Photoluminescence Signal from Pulsed N_2 Laser Excitation (337.1 nm) of SnO vs Time for Several Total System Pressures

REFERENCES

1. D. G. Sutton and S. N. Suchard, *Appl. Opt.* 14, 1898 (1975).
2. W. Felder and A. Fontijn, *Chem. Phys. Lett.* 34, 398 (1975).
3. See e.g., C. R. Jones and H. P. Broida, *J. Chem. Phys.* 60, 4369 (1974), or R. W. Field, A. D. English, T. Tanaka, D. O. Harris, and D. A. Jennings, *J. Chem. Phys.* 59, 2191 (1973).
4. An. N. Nesmeyanov, Vapour Pressure of the Elements (Academic Press, New York, 1963), p. 272.
5. G. A. Capelle and J. Brom, *J. Chem. Phys.* 63, 5168 (1975).
6. B. Meyer, J. J. Smith, and K. Spitzer, *J. Chem. Phys.* 53, 3616 (1970).
7. M. J. Linevsky and R. A. Carabetta, Chemical Laser Systems, Final Technical Report, 1 April 1975 - 15 Oct. 1975, General Electric Space Sciences Laboratory, Philadelphia, Pa.
8. C. Linton and H. P. Broida, *J. Mol. Spectrosc.* (to be published).
9. A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules (Chapman and Hall, London, 1968), 3rd ed.
10. Spectroscopic Data Relative to Diatomic Molecules, International Tables of Selected Constants, ed. B. Rosen (Pergamon, New York, 1970).
11. E. W. Deutsch and R. F. Barrow, *Nature* 201, 815 (1964).
12. M. M. Joshi and R. Yamdagni, *Indian J. Phys.* 16, 275 (1967).
13. R. C. Oldenborg, C. R. Dickson, and R. N. Zare, *J. Mol. Spectrosc.* 58, 283 (1975).
14. G. Hager, R. Harris, and S. G. Hadley, *J. Chem. Phys.* 63, 2810 (1975).
15. A. Fontijn, Aerochem Research Laboratories, Princeton, N.J., (private communication).

16. D. J. Eckstrom, S. A. Edelstein, D. L. Huestis, B. E. Perry, and S. W. Benson, Stanford Research Institute Semiannual Technical Report No. 3, SRI 75-44 (September 1975).
17. W. Felder, Aerochem Research Laboratories, Princeton, N.J., (private communication).

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