

## BEAM-GAS CHEMILUMINESCENT REACTIONS OF Eu AND Sm WITH O<sub>3</sub>, N<sub>2</sub>O, NO<sub>2</sub> AND F<sub>2</sub><sup>\*</sup>

C.R. DICKSON and R.N. ZARE

*Department of Chemistry, Columbia University, New York, N.Y. 10027, USA*

Received 21 November 1974

Studies are made of the visible chemiluminescence resulting from the reaction of an atomic beam of samarium or europium with O<sub>3</sub>, N<sub>2</sub>O, NO<sub>2</sub> and F<sub>2</sub> under single-collision conditions ( $\sim 10^{-4}$  torr). The spectra obtained for SmO, EuO, SmF, and EuF are considerably more extensive than previously observed. The variation of the chemiluminescent intensity with metal flux and with oxidant flux is investigated, and it is concluded that the reactions are bimolecular. From the short wavelength cutoff of the chemiluminescent spectra, the following lower bounds to the ground state dissociation energies are obtained:  $D_0^0(\text{SmO}) \geq 135.5 \pm 0.7$  kcal/mole,  $D_0^0(\text{EuO}) \geq 131.4 \pm 0.7$  kcal/mole,  $D_0^0(\text{SmF}) \geq 123.6 \pm 2.1$  kcal/mole, and  $D_0^0(\text{EuF}) \geq 129.6 \pm 2.1$  kcal/mole. Using the Clausius–Clapeyron equation, the latent heats of sublimation are found to be  $\Delta H_{1052}(\text{Eu}) = 42.3 \pm 0.7$  kcal/mole for europium and  $\Delta H_{1084}(\text{Sm}) = 47.9 \pm 0.7$  kcal/mole for samarium. Total phenomenological cross sections are determined for metal atom removal. Relative photon yields per product molecule are calculated from the integrated chemiluminescent spectra and it is found that  $\text{Sm} + \text{F}_2 \rightarrow \text{SmF}^* + \text{F}$  is the brightest reaction. The comparison of the photon yields under single-collision conditions with those at several torr shows that energy transfer collisions play an important role in the mechanism for chemiluminescence at the higher pressures. A simple model is presented which explains the larger photon yields of the Sm reactions compared to the Eu reactions in terms of the greater number of electronic states correlating with the reactants in the case of samarium.

### 1. Introduction

Very little is known about the spectroscopy of the diatomic oxides and fluorides of samarium and europium. In general, these high temperature species are expected to have very rich and complex spectra because of the predicted large number of low-lying electronic states of high multiplicity. This is illustrated by considering the number and symmetry types of states arising from the ground-state separated atoms. For SmO and SmF 36 states and 24 states, respectively, correlate with the ground state of samarium ( $\text{Sm } 7\text{F}$ ) and the ground state of oxygen ( $\text{O } 3\text{P}$ ), and the ground state of fluorine ( $\text{F } 2\text{P}^0$ ). For europium ( $\text{Eu } 8\text{S}^0$ ) the number and symmetry types of states are much less extensive: there are only 6 states ( $6,8,10\Sigma^+$  and  $6,8,10\Pi$ ) of EuO and 4 states ( $7,9\Sigma^-$ ,  $7,9\Pi$ ) of EuF which correlate with the ground-state atoms. Since samarium and europium both have low-lying atomic states, many more diatomic states are expected to exist which have visible band systems. Indeed, the symmetry of the ground states of the four species, SmO, EuO, SmF, and EuF, are presently unknown.

No spectra appear to have been previously reported for SmF and EuF. The spectra of SmO and EuO have been obtained in emission from arc and flame studies of the Sm and Eu salts [1–3]. More extensive spectra of EuO have been obtained by Drapatz et al. [4] from artificially produced metal vapor clouds released in the upper atmosphere.

Recently, the chemiluminescent emission from SmO and EuO have been recorded by Edelstein et al. [5] who investigated the reactions of Sm and Eu with various oxidants at pressures of a few torr. These workers report maximum photon yields of 35% for SmO formed from  $\text{Sm} + \text{N}_2\text{O}$  and 20% for EuO formed from  $\text{Eu} + \text{N}_2\text{O}$ . These studies are presently being extended to SmF and EuF; photon yields for the  $\text{Sm} + \text{F}_2$  reaction appear to be greater than 50% [6]. The significance of these high photon yields (photons produced per metal atom consumed) is that these reactions of Sm and Eu may provide the basis for a chemically-powered visible laser system. Consequently, a knowledge of the spectroscopy of SmO, SmF, EuO, and EuF is highly desired in order to understand the kinetics of these reaction systems.

In this paper we present a survey of the reactions of Sm and Eu with O<sub>3</sub>, N<sub>2</sub>O, NO<sub>2</sub>, and F<sub>2</sub> under single-collision conditions using a beam-gas arrangement [7]. The spectra we obtain show considerably more structure than those at higher oxidant pressures. The intensity of the chemiluminescence at a fixed wavelength is studied as a function of both oxidant pressure and metal beam flux. From these measurements we find that the chemiluminescent reactions proceed by a bimolecular mechanism in the pressure range near 10<sup>-4</sup> torr. We also determine the total phenomenological cross sections for metal atom removal, the relative cross sections for photon production, and the latent heat of sublimation for Eu and Sm. In addition, the short wavelength limit of the chemiluminescent spectra provides a lower bound to the ground state dissociation energy of the diatomic product. A comparison is made of our values for SmO, SmF, EuO, and EuF with those determined by thermodynamic means [8,9].

## 2. Experimental

The beam apparatus, LABSTAR, has been previously described [7]. Recently, the apparatus was modified to include a water-cooled Astro-oven (Astro Industries, Inc.) which resistively heats a cylindrical graphite tube containing a cylindrical graphite crucible with an aperture of 0.2 cm in diameter. The entire crucible-heater arrangement was surrounded by three concentric tantalum heat shields. The samarium powder (99.99% purity) was obtained from Alpha-Ventron Corp. The europium metal was provided by K.W. Michel and its purity was unknown. The metals are resistively heated inside the graphite crucible to a pressure of 0.1 torr. At this vapor pressure, the beam flux in the reaction zone is estimated to be  $\lesssim 10^{16}$  atoms cm<sup>-2</sup> s<sup>-1</sup>. No provisions are made to collimate the oxidant gas beam and it essentially filled the entire reaction chamber. At low oxidant pressures ( $\approx 10^{-4}$  torr) the chemiluminescent reactions are produced by single collisions. Since the ionization gauge was located away from the reaction zone, the recorded pressure may be lower than that in the reaction zone by  $\approx 50\%$ . The ozone is generated with a Welsbach ozonizer and is adsorbed onto silica gel cooled to the temperature of a dry ice and acetone slush. Before using the ozone,

any oxygen produced by the decomposition of ozone was removed by pumping on the trap. The oxidants N<sub>2</sub>O, NO<sub>2</sub>, and F<sub>2</sub> were used as bottled by Matheson Corp. A ballast tank filled with these oxidants was used to maintain a constant pressure as the gas is bled into the reaction chamber through a micrometer needle valve. Both ozone and fluorine are extremely reactive which may have affected the pressure readings by the ionization gauge. In the case of fluorine it is estimated that the pressure readings are reproducible to within a factor of two.

The chemiluminescence is detected with a 1 meter Interactive Technology Czerny-Turner spectrometer operated in first order with a Bausch and Lomb 1200 groove/mm grating blazed at 5000 Å. Most spectra presented in this paper were taken with a slit width of 500  $\mu$  corresponding to a resolution of 5 Å. A cooled Centronic S-20 photomultiplier is attached to the exit slits of the spectrometer. The photomultiplier signal serves as the input to a Keithley 417 fast picoammeter whose output drives a Hewlett-Packard 7100 B chart recorder. All of the spectra presented are uncorrected for the variation of detector response with wavelength.

The entire optical detection system was calibrated with a 200 W quartz-iodine lamp (General Electric model 6.6A/T4Q/1C1-200W). When operated at 6.5 A, the spectral irradiance (energy s<sup>-1</sup> cm<sup>-2</sup> nm<sup>-1</sup>) at 43 cm from the axis of the lamp filament is given by Stair et al. [10]. A relative calibration was made by comparing the spectral irradiance of the standard lamp to the output obtained through the entire optical detection system. The relative number of photons s<sup>-1</sup> cm<sup>-2</sup> produced by the chemiluminescence was obtained from the area of the chemiluminescence spectra corrected for the variation of number of photons per unit energy interval as a function of wavelength.

## 3. The appearance of the spectra

Fig. 1 shows the rapid scans at 500 Å/min of the chemiluminescent spectra for the reactions of Sm with O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub>. The spectra have two prominent features, one at 4000–5500 Å and another at 5500–7500 Å. These features may correspond to different spectroscopic states. The spectra produced from the reaction of Sm with O<sub>3</sub> and N<sub>2</sub>O show little structure. The spectrum produced by the reaction of

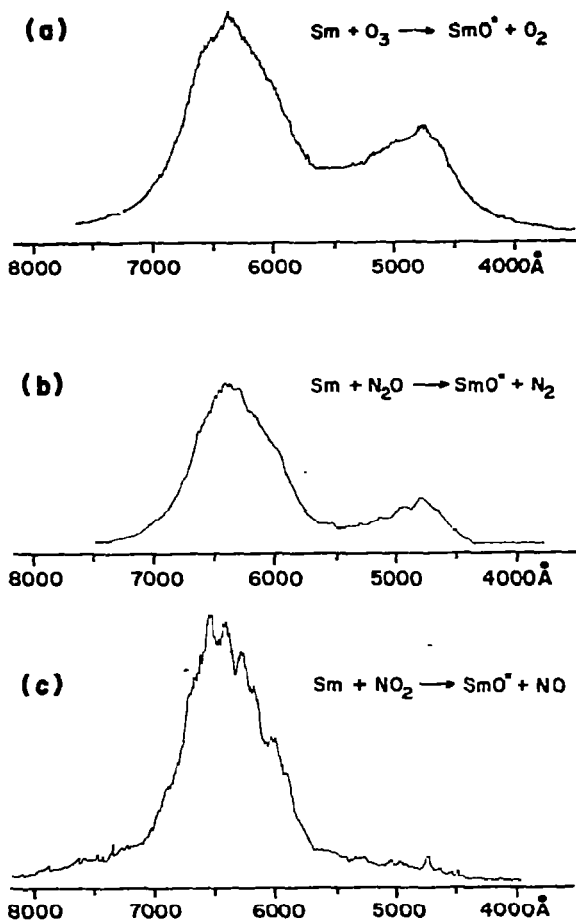


Fig. 1. The chemiluminescent spectra of the reactions (a)  $\text{Sm} + \text{O}_3 \rightarrow \text{SmO}^* + \text{O}_2$ , (b)  $\text{Sm} + \text{N}_2\text{O} \rightarrow \text{SmO}^* + \text{N}_2$ , and (c)  $\text{Sm} + \text{NO}_2 \rightarrow \text{SmO}^* + \text{NO}$ . All spectra were taken at a resolution of 5 Å and at a scan rate of 500 Å/min.

Sm with NO<sub>2</sub> contains a number of sharp peaks and band heads. The feature at 4000–5500 Å is not as large as in the spectra produced by the reaction of Sm with O<sub>3</sub> and N<sub>2</sub>O but some structure does appear. The color to the eye for the reaction of Sm with the oxidants O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub> was white-red, crimson red, and very deep red, respectively. As the oxidants are ranked in increasing bonding energy (O<sub>3</sub> < N<sub>2</sub>O < NO<sub>2</sub>) fig. 1 shows that (1) the intensity of the higher-energy blue feature decreases with respect to the lower-energy red feature, and (2) increasing structure appears in the spectra.

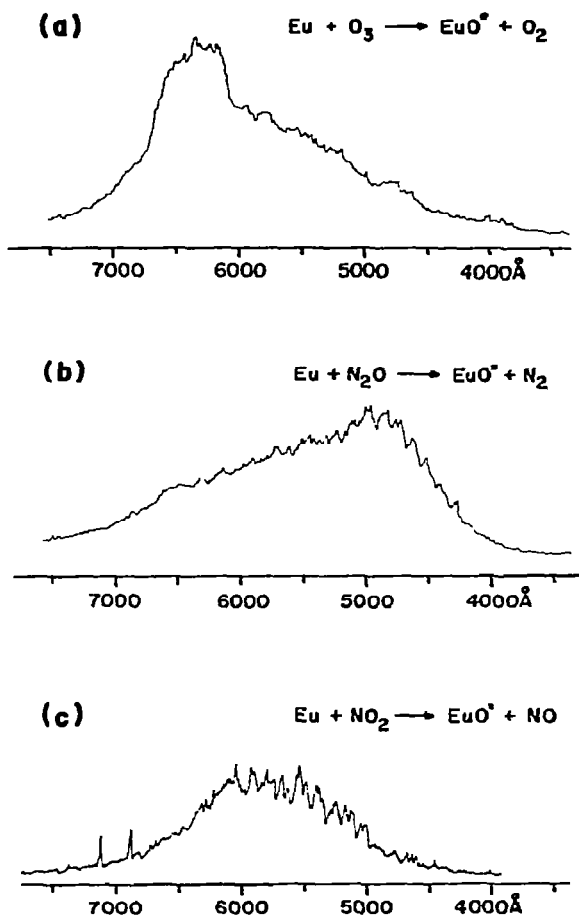


Fig. 2. The chemiluminescent spectra of the reactions (a)  $\text{Eu} + \text{O}_3 \rightarrow \text{EuO}^* + \text{O}_2$ , (b)  $\text{Eu} + \text{N}_2\text{O} \rightarrow \text{EuO}^* + \text{N}_2$ , and (c)  $\text{Eu} + \text{NO}_2 \rightarrow \text{EuO}^* + \text{NO}$ . All spectra were taken at a resolution of 5 Å and a scan rate of 500 Å/min.

Fig. 2 shows analogous rapid scans at 500 Å/min of the chemiluminescent spectra for the reactions of Eu with O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub>. The spectra produced by the reaction of Eu with O<sub>3</sub> displayed little structure, although Eu with N<sub>2</sub>O and NO<sub>2</sub> had many sharp band heads. The reaction of Eu with N<sub>2</sub>O contained a large amount of rotational structure. This is illustrated in fig. 3 taken at a scan speed of 100 Å/min and with a resolution of 1.5 Å. The spectroscopic analysis of this spectra is presently under consideration. The color to the eye for the reaction of Eu with O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub> was lemon yellow, white with blue tinge,

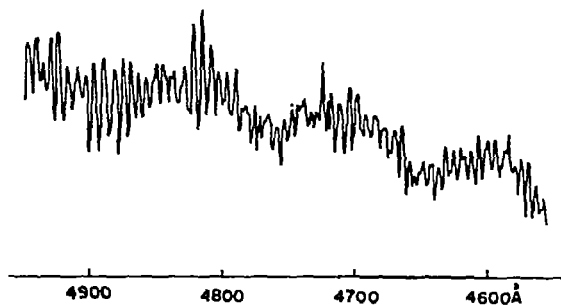


Fig. 3. The chemiluminescent spectra of  $\text{Eu} + \text{N}_2\text{O} \rightarrow \text{EuO}^* + \text{N}_2$  taken at a resolution of 1 Å and a scan rate of 100 Å/min.

and lemon yellow, respectively. Once again the spectra in fig. 2 show increasing structure as the oxidant bond energy increases, but there is no simple shift of intensity from the blue to the red, as in fig. 1.

The spectra obtained by the chemiluminescent reactions of Eu and Sm with F<sub>2</sub> are shown in figs. 4 and 5. While both spectra appear to have only slight structure, it was possible to obtain more detailed structure by observing the less intense portion of the spectra with a more sensitive detector response. This is shown in the insert to fig. 5. These reactions are so intense that most of the structure was lost in the attenuation necessary to display the spectra in figs. 4 and 5. The color to the eye for the reaction of Eu with F<sub>2</sub> was blue with a red tinge at the flame center, while the reaction of

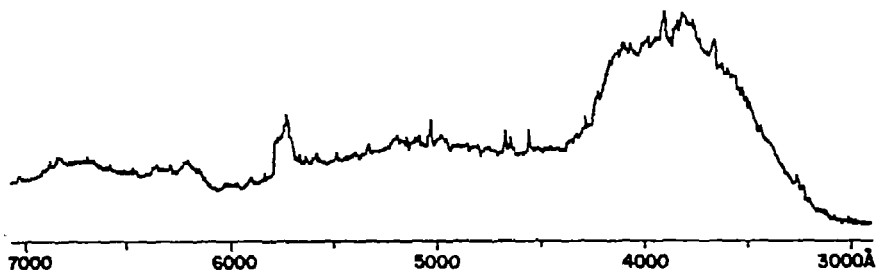
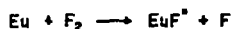


Fig. 4. The chemiluminescent spectra of  $\text{Eu} + \text{F}_2 \rightarrow \text{EuF}^* + \text{F}$  taken at a resolution of 5 Å and a scan rate of 500 Å/min.

Sm with F<sub>2</sub> was a deep crimson-violet color.

It is encouraging to find that the metal oxide and metal fluoride spectra of Eu and Sm appear to be considerably simpler than was expected from the possible number of electronic states. We are hopeful that a spectroscopic analysis can be made of these bands, since they seem to result from one or two electronic transitions. The observation of what appears to be rotational structure in EuO further supports this optimistic picture.

#### 4. Reaction molecularity and kinetics

##### 4.1. Dependence of intensity on metal flux

As the temperature of the metal oven is increased, the vapor pressure,  $P$ , of the metal increases according to the Clausius-Clapeyron relation

$$d \ln P/d(1/T) = -\Delta H_T/R, \quad (1)$$

where  $\Delta H_T$  is the latent heat of sublimation at the temperature  $T$  (taken to be the mean of the temperature range). We have investigated the chemiluminescence intensity at a fixed oxidant pressure and at a fixed wavelength when the oven temperature is varied. The results of this study are presented in fig. 6 where the logarithm of the chemiluminescence intensity is plotted versus the reciprocal of the temperature for the reaction of Sm with O<sub>3</sub>. We conclude that these reactions are first order in the metal atom flux from the linearity of these plots. Similar studies were carried out for Eu + F<sub>2</sub> and Sm + F<sub>2</sub> (not shown) in

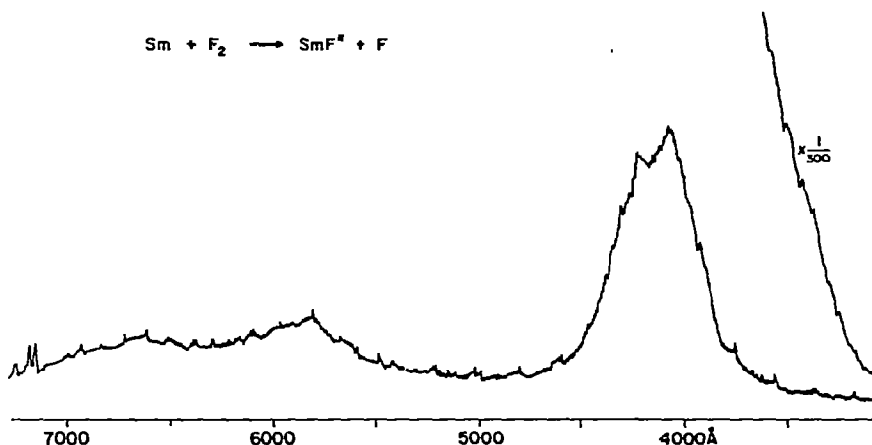


Fig. 5. The chemiluminescent spectra of  $\text{Sm} + \text{F}_2 \rightarrow \text{SmF}^* + \text{F}$  taken at a resolution of 5 Å and a scan rate of 500 Å/min. The upper trace shows more structure between 3000–3500 Å for an identical scan when the detector sensitivity is increased by a factor of 300.

which the intensity also followed a linear relation with metal flux. Although the reactions  $\text{Eu} + \text{N}_2\text{O}$  and  $\text{Eu} + \text{NO}_2$  were not studied in this manner (because the supply of europium was exhausted), we believe that one and only one metal atom participates in each chemiluminescent reaction.

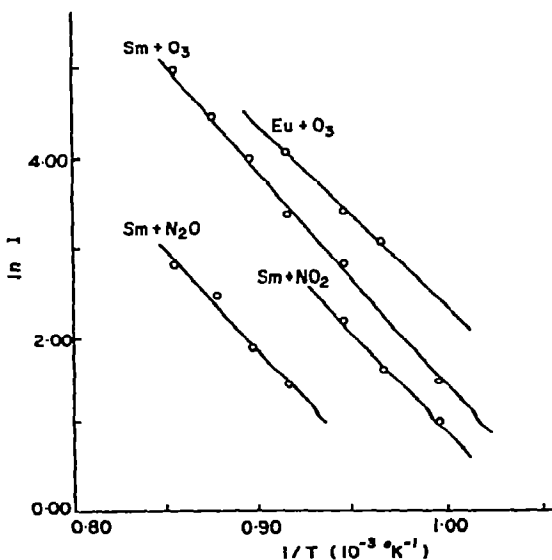


Fig. 6. Plot of the logarithm of the chemiluminescent intensity versus the reciprocal of the metal oven temperature for the reactions of Sm with O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub> and Eu with O<sub>3</sub>. The oxidant pressure was fixed at  $2 \times 10^{-4}$  torr and the wavelength was fixed at 6250 Å.

Provided the reaction rate does not change appreciably with velocity (temperature), the slopes of the straight lines in fig. 6 give the latent heat of sublimation. We obtain in the temperature range 1000 to 1160 K for samarium

$$\Delta H_{1084}(\text{Sm}) = 47.9 \pm 0.7 \text{ kcal/mole}, \quad (2)$$

and in the temperature range 1031 to 1075 K for europium

$$\Delta H_{1052}(\text{Eu}) = 42.3 \pm 0.7 \text{ kcal/mole}. \quad (3)$$

In table 1 these results are compared with the values obtained by other workers [11] for slightly different

Table 1  
The latent heats of sublimation for samarium and europium

Metal	Investigator	Temperature range (K)	$\Delta H_T$ (kcal/mole)
Samarium	Savage, Hudson and Spedding [11a]	700–950	$48.66 \pm 0.4$
	Haberman and Daane [11c]	885–1222	$49.35 \pm 0.14$
	Present study	1000–1160	$47.9 \pm 0.7$
Europium	Haberman and Daane [11c]	696–900	41.1
	Tulson, Hudson, and Spedding [11b]	693–751	$42.04 \pm 0.25$
	Present study	1031–1075	$42.3 \pm 0.7$

temperature ranges. The excellent agreement lends credence to our assumption that the chemiluminescent reactions have no appreciable activation energy.

#### 4.2. Dependence of intensity on oxidant pressure

For all of the reactions, the intensity of the chemiluminescence at a fixed wavelength and at a fixed oven temperature was studied as a function of oxidant pressure. The plot of the intensity versus oxidant pressure is linear in the low pressure region below  $10^{-4}$  torr (see figs. 7–9). The linearity of these plots indicate that all of the chemiluminescence reactions proceed by a simple bimolecular mechanism since reactions are also first order in metal flux, as discussed in the previous section. At higher pressures the plots reflect the attenuation of the metal beam between the entrance port of the reaction chamber and the reaction zone viewed by the spectrometer. All of the curves in figs. 7 and 8 were assumed to obey a  $p \exp(-\alpha p)$  relationship where  $p$  is the oxidant pressure. The linear term in  $p$  describes the formation of excited state molecules and the exponential term  $\exp(-\alpha p)$  describes the attenuation of the metal beam by the oxidant. The attenuation parameter  $\alpha$  in  $\text{torr}^{-1}$  is related to the total phenomenological cross section for metal beam re-

moval  $\sigma$  in  $\text{\AA}^2$  by

$$\alpha = 1.33 \times 10^{-13} l \sigma / kT, \quad (4)$$

where  $l$  is the beam path length (4.5 cm) in the reaction chamber from the port of entry to the reaction zone viewed by the spectrometer,  $k$  is Boltzmann's constant in  $\text{erg K}^{-1}$ , and  $T$  is the absolute temperature (300 K for the oxidants). The constant  $1.333 \times 10^{-13}$  has units of  $\text{dyne torr}^{-1} \text{\AA}^{-2}$ . The maxima in the plots of  $I$  versus  $p$  occur at

$$p_{\max} = 1/\alpha. \quad (5)$$

Thus, the attenuation parameter  $\alpha$  can easily be estimated from the position of maximum intensity; then  $\sigma$  can be determined from  $\alpha$  using eq. (4). The cross sections, listed for each of the reactions in table 2, are phenomenological cross sections comprising all attenuation effects. These may be regarded as upper limits to the reaction cross sections.

For the reactions of Sm and Eu with fluorine, the deviation of the plots in fig. 9 from the  $p \exp(-\alpha p)$  relationship reflects the high reactivity of fluorine with the pressure gauge. However, fig. 10 clearly shows that the plot of intensity versus fluorine pressure is linear for low pressures (below  $10^{-4}$  torr) which indicates a bimolecular mechanism for the reac-

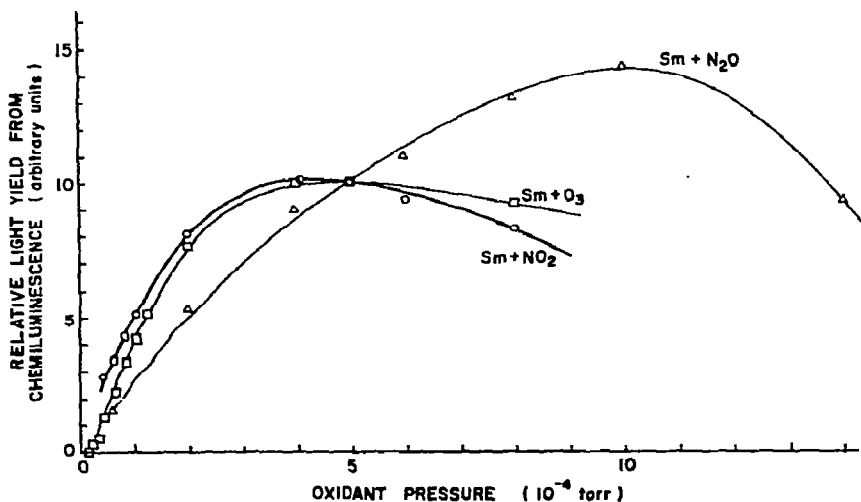


Fig. 7. Relative chemiluminescent intensity versus oxidant pressure for the reactions of Sm with O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub>. The metal oven temperature and wavelength were fixed at 1150 K and 6250 Å, respectively. At an oxidant pressure of  $5 \times 10^{-4}$  torr, the relative intensity for each of the reactions was normalized to 10. The actual phototube output (in  $\mu\text{A}$ ) at  $5 \times 10^{-4}$  torr is 3.70, 0.28, 0.27 for the reactions of Sm with O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub>, respectively.

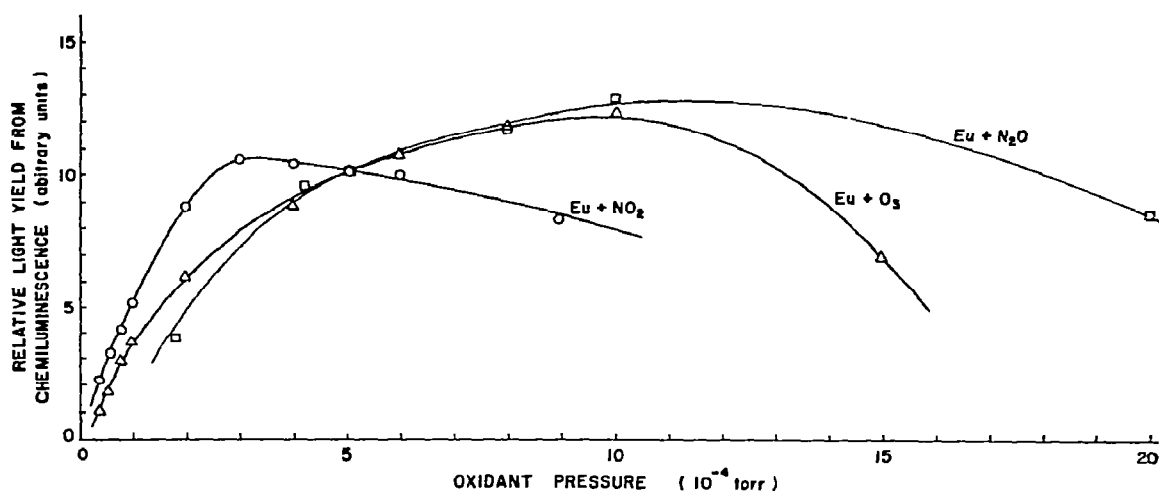


Fig. 8. Relative chemiluminescent intensity versus oxidant pressure for the reactions of Eu with O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub>. The metal oven temperature and wavelength were fixed at 1000 K and 5500 Å, respectively. At an oxidant pressure of  $5 \times 10^{-4}$  torr, the relative intensity for each of the reactions was normalized to 10. The actual phototube output (in  $\mu\text{A}$ ) at  $5 \times 10^{-4}$  torr is 0.37, 0.32, and 0.24 for the reactions of Eu with O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub>, respectively.

tions of Sm and Eu with fluorine. If the curvature in the plot for Eu + F<sub>2</sub> in fig. 9 were due to a  $p^2 \exp(-ap)$  relationship the low pressure plot of fig. 10 would be quadratic instead of linear. Thus, the curvature in fig. 9

appears to be caused by the reactivity of fluorine with the ionization gauge.

Since the pressure read by the ionization gauge may be systematically lower than that in the reaction

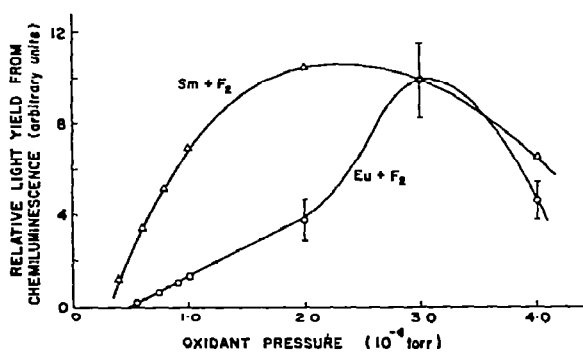


Fig. 9. Relative chemiluminescent intensity versus oxidant pressure for the reactions of Sm and Eu with F<sub>2</sub>. The metal oven temperature was fixed at 1150 K for Sm and 1000 K for Eu. For both reactions, the wavelength was fixed at 4000 Å. At a pressure of  $3 \times 10^{-4}$  torr, the relative intensity was normalized to 10. The actual phototube output (in  $\mu\text{A}$ ) at  $3 \times 10^{-4}$  torr is 5.00 and 10.00 for the reactions Eu + F<sub>2</sub>, respectively. The error bars represent the spread in intensity measurements for a given nominal pressure reading.

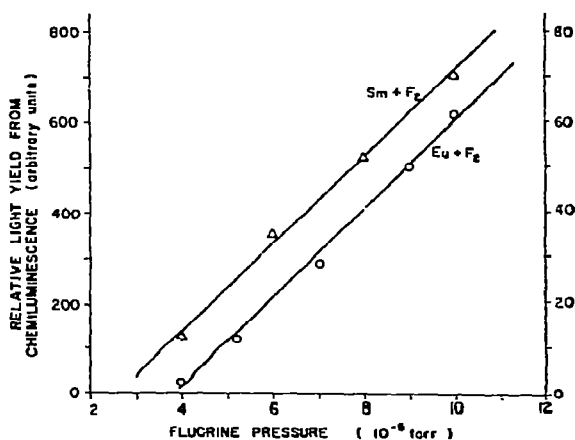


Fig. 10. Relative chemiluminescent intensity versus F<sub>2</sub> pressure in the low pressure region ( $< 10^{-4}$  torr) for the reactions of Sm and Eu with F<sub>2</sub>. The scale on the left pertains to the Sm + F<sub>2</sub> reaction, while the scale on the right pertains to the Eu + F<sub>2</sub> reaction.

Table 2

The ratio of total phenomenological cross sections for the reactions of Sm and Eu with F<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, and NO<sub>2</sub>. All values are normalized to the reaction Sm + F<sub>2</sub> → SmF\* + F which has the largest cross section (314 Å<sup>2</sup>)

Metal	Oxidant			
	F <sub>2</sub>	O <sub>3</sub>	N <sub>2</sub> O	NO <sub>2</sub>
Sm	1.00	0.44	0.19	0.50
Eu	0.67	0.20	0.20	0.67

zone by ≈ 50%, the values of α may be systematically higher by ≈ 50%. However, for the reactions of Sm and Eu with fluorine, α may be substantially in error by as much as a factor of two since the ionization gauge readings may have been low by a corresponding factor of two (see experimental section).

#### 4.3. Relative photon yields for excited state production

The branching ratio between ground state and excited state products is an important quantity for understanding the reaction dynamics as well as for assessing the promise of these chemiluminescent reactions as the active medium of a visible laser system. While we did not determine absolute photon yields, i.e., number of photons produced per metal atom consumed in these studies, we have obtained relative photon yields from the integrated chemiluminescent spectra between 3000–8000 Å. By correcting for the variation of photon number with wavelength and by using a

quartz-iodine lamp for relative standardization, we have obtained the relative number of photons s<sup>-1</sup> cm<sup>-2</sup>. By dividing the relative photon yield by the total phenomenological cross section given in table 2, we obtain the relative photon yield per product molecule formed.

Table 3 presents these results and compares them with the relative photon yields at high pressures (several torr) obtained by Edelstein et al. [6]. All the values were normalized to the reaction of Sm + F<sub>2</sub> since it was the brightest. A comparison of reactions of Sm with O<sub>3</sub> and N<sub>2</sub>O shows that collisions at high pressures increase the relative photon yield for the reaction of Sm with N<sub>2</sub>O, but decrease the relative photon yield for the reaction of Sm with O<sub>3</sub>. At low pressures the relative photon yields of Sm + F<sub>2</sub>, Sm + O<sub>3</sub>, and Eu + F<sub>2</sub> are all nearly equal. The relative photon yield for the reaction of Eu + F<sub>2</sub> at high pressures has dropped considerably indicating that collisions enhance the photon yield for Sm + F<sub>2</sub> much more than for Eu + F<sub>2</sub>. Although we do not obtain absolute branching ratios in this study, we can determine relative branching ratios which are proportional to the relative photon yields listed in table 3. Once again, it is apparent that the total cross section for the reaction of Sm or Eu with NO<sub>2</sub> is quite large, but the production of excited products for these reactions is very small.

The similarity of our chemiluminescent spectra with those obtained by Edelstein et al. [6] at higher pressures shows that in both cases the emitters are the same, namely, the diatomic metal fluorine or oxide. The question arises why are the photon yields

Table 3

Relative photon yields for the chemiluminescent reactions of Sm and Eu with F<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O and NO<sub>2</sub>

Metal	Relative number of photons per product molecule						
	Oxidant at ~ 10 <sup>-4</sup> torr <sup>a)</sup>				Oxidant at several torr <sup>b)</sup>		
	F <sub>2</sub>	O <sub>3</sub>	N <sub>2</sub> O	NO <sub>2</sub>	F <sub>2</sub>	O <sub>3</sub>	N <sub>2</sub> O
Samarium	1.00	0.88	0.28 <sup>c)</sup>	0.074	1.00	0.13	0.59
Europium	0.92	0.34	0.18	0.0074	0.25	0.078	0.039

a) The relative photon yields pertain to visible emission between 3000–8000 Å. For the reactions of Sm + F<sub>2</sub> and Eu + F<sub>2</sub> a peak began to appear beyond 8000 Å in the corrected spectra. Since the response of the S-20 phototube is extremely low in this region, this peak may not be real and was not included in our relative photon yields.

b) Ref. [6]. These results pertain to the visible emission between 2000–8500 Å.

c) We find a preliminary absolute photon yield of 0.3% for this reaction.



of the Sm reactions so much larger than those of the Eu reactions at pressures of a few torr. The fact that  $\text{Sm} + \text{F}_2$ ,  $\text{Sm} + \text{O}_3$ , and  $\text{Eu} + \text{F}_2$  have comparable photon yields under single-collision conditions, implies that energy transfer processes rather than subsequent chemical reactions, are populating the  $\text{SmO}^*$  and  $\text{SmF}^*$  states much more than  $\text{EuO}^*$  or  $\text{EuF}^*$ . We suggest that these results may be rationalized based on the larger number of excited states present for  $\text{SmO}$  and  $\text{SmF}$  compared to  $\text{EuO}$  and  $\text{EuF}$ .

A very crude model for these chemiluminescent reactions is that the excess energy is partitioned between internal energy and translational energy to about the same extent for each reaction. For lack of better information, the internal energy is assumed to be divided statistically among the possible electronic states correlating with the ground-state reactants. Thus, the internal energy appears in either high vibrational levels of the ground or in low to moderate vibrational levels of the excited states. Subsequent collisions rapidly transfer energy among the electronic states, and the electronic state with the shortest radiate lifetime acts as a "funnel" through which the reaction exothermicity "pours". In this model, Sm with its <sup>7</sup>F ground state leads to the production of many more excited state products than Eu with its <sup>8</sup>S ground state. Indeed, we imagine that only one of the seven possible orientations of the F state correlates with the ground state product for the Sm reactions. This picture suggests that other favorable candidates for large photon yields at pressures of a few torr will be open-shell atoms in high L states. A quick survey of the periodic table reveals that the transition metals, the lanthanides, and the actinides provide some candidate systems satisfying the above criteria.

## 5. Dissociation energies

It is possible to set lower bounds to bond dissociation energies from a study of the spectra produced from the chemiluminescent reactions under single-collision conditions [12]. From the application of energy balance to the reactions  $\text{Sm} + \text{NO}_2 \rightarrow \text{SmO} + \text{NO}$  and neglecting the final relative translational energies, the inequality

$$D_0^0(\text{SmO}) \geq D_0^0(\text{ON-O}) + E_{\text{int}}(\text{SmO}) - E_{\text{int}}(\text{Sm}) - E_{\text{int}}(\text{NO}_2) - E_{\text{trans}}^i \quad (6)$$

provides a lower bound to  $D_0^0(\text{SmO})$ .

In eq. (6)  $E_{\text{int}}(\text{Sm})$ ,  $E_{\text{int}}(\text{NO}_2)$ , and  $E_{\text{int}}(\text{SmO})$  are the average internal energies of Sm,  $\text{NO}_2$ , and  $\text{SmO}$ , respectively, measured from their lowest energy levels, and  $E_{\text{trans}}^i$  is the initial relative translational energy, measured in the center-of-mass frame. The value of  $E_{\text{int}}(\text{NO}_2)$  is calculated to be 0.600 kcal/mole where we have taken into account the average rotational energy ( $\frac{3}{2} RT$ ) at  $T = 300$  K but have regarded the average vibrational energy as negligible. The dissociation energy of  $\text{NO}_2$  is taken to be  $D_0^0(\text{ON-O}) = 71.83$  kcal/mole [13]. The initial relative translational energy is estimated from the expression [12]

$$E_{\text{trans}}^i = \frac{3}{2} kT_{\text{eff}} \quad (7)$$

where

$$T_{\text{eff}} = \frac{T(\text{Sm})m(\text{NO}_2) + T(\text{NO}_2)m(\text{Sm})}{m(\text{NO}_2) + m(\text{Sm})} \quad (8)$$

Here  $T(\text{Sm}) = 1106$  K,  $T(\text{NO}_2) = 300$  K,  $m(\text{Sm}) = 2.49 \times 10^{-22}$  g, and  $m(\text{NO}_2) = 7.64 \times 10^{-23}$  g, yielding  $E_{\text{trans}}^i = 1.41$  kcal/mole. From the short wavelength cutoff ( $\lambda = 4250$  Å) in the chemiluminescent spectrum, shown in fig. 1c,  $E_{\text{int}}(\text{SmO})$  is determined to be 67.65 kcal/mole. This is a lower bound to  $E_{\text{int}}(\text{SmO})$  for we have assumed here that the short wavelength cutoff corresponds to a transition terminating on the  $v'' = 0$  level of the  $\text{SmO}$  ground state. Finally, the internal energy of the Sm beam is determined by the average thermal distribution of the fine structure levels of the  $\text{Sm}(^7\text{F})$  state for  $T = 1106$  K,

$$E_{\text{int}}(\text{Sm}) = \frac{\sum_i \epsilon_i g_i \exp(-\epsilon_i/kT)}{\sum_i g_i \exp(-\epsilon_i/kT)} \quad (9)$$

The energy  $\epsilon_i$  for each atomic energy level, measured with respect to the lowest level  $^7\text{F}_0$ , was taken from the data of Albertson [14]. The multiplicity  $g_i$  is given by  $2J+1$ . Using eq. (9) the value of  $E_{\text{int}}(\text{Sm})$  is determined to be 2.21 kcal/mole.

With these values, the lower bound to the  $\text{SmO}$  dissociation energy is found from eq. (6) to be

$$D_0^0(\text{SmO}) \geq 135.5 \pm 0.7 \text{ kcal/mole}, \quad (10)$$

where the error estimate includes the uncertainties in  $E_{\text{trans}}^i$  (the dominant contribution) and the other

terms used in evaluating eq. (6). In the same manner, we find from the short wavelength cutoffs for the reactions Eu + NO<sub>2</sub>, Sm + F<sub>2</sub>, and Eu + F<sub>2</sub> the lower bounds

$$D_0^0(\text{EuO}) \geq 131.4 \pm 0.7 \text{ kcal/mole,}$$

$$D_0^0(\text{SmF}) \geq 123.6 \pm 2.1 \text{ kcal/mole,}$$

and

$$D_0^0(\text{EuF}) \geq 129.6 \pm 2.1 \text{ kcal/mole.} \quad (11)$$

In the latter two cases,  $D_0^0(\text{F}_2)$  is taken as  $37.10 \pm 0.85$  kcal/mole [15]. For the Eu reactions,  $E_{\text{int}}$  is taken as zero since the ground state of Eu is  $^8S_{7/2}$ . The above dissociation energies for SmO and EuO are in good agreement with those obtained by Ames et al. [8] from Knudson effusion techniques and spectrometric oxygen-exchange reaction studies, namely,  $D_0^0(\text{SmO}) = 142 \pm 3$  kcal/mole and  $D_0^0(\text{EuO}) = 133.8 \pm 3$  kcal/mole. The above dissociation energies for SmF and EuF are also in reasonable agreement with the values obtained by Zmbov and Margrave [9] from Knudson effusion studies, namely,  $D_0^0(\text{SmF}) = 126.9 \pm 4.4$  kcal/mole and  $D_0^0(\text{EuF}) = 126 \pm 4.1$  kcal/mole.

It must be emphasized that the dissociation energies we have obtained from the chemiluminescent spectra are strictly lower bounds to the true value. In particular, the short wavelength cutoff is assumed to be caused by a transition to the lowest vibrational level in the ground state of the chemiluminescent species. If the short wavelength cutoff corresponds to a transition terminating on a higher vibrational level, then the energy difference between this level and  $v'' = 0$  must be added to the dissociation energy. A spectroscopic analysis of the chemiluminescent spectra is required in order to improve these estimates of the ground state dissociation energies.

It is interesting to note that the bond energies for EuO and SmO exceed that of O<sub>2</sub>. Thus, the persistence of Eu atoms in high altitude releases is not explained solely on thermodynamic grounds [4]. The reaction of Sm and Eu with O<sub>2</sub> is only exothermic by 15 kcal/mole and 11 kcal/mole, respectively. Consequently, these reactions are not expected to be sufficiently exothermic to yield electronic excited products that emit in the visible. Indeed, no chemiluminescence was observed for the reactions of Eu and Sm with O<sub>2</sub> under our operating pressures corresponding to single-collisions conditions.

## Acknowledgement

We thank Dr. K.W. Michel (Max-Planck-Institut für Physik und Astrophysik, Garching, Germany) who kindly supplied us with europium samples for these studies. We are also grateful to Dr. D.J. Eckstrom, Dr. S. Edelstein, Dr. D. Huestis, and Dr. S. Benson (Stanford Research Institute, Menlo Park, California) who communicated to us their photon yield measurements prior to publication. This work is supported by the Army Research Office (Durham) under grant DA-ARO-D-31-124-73-G147.

## References

- [1] A. Gatterer and J. Junkes, Molecular spectra of metallic oxides (Specola Vaticana, 1957).
- [2] R. Mavrodineau and H. Boiteaux, Flame spectroscopy (Wiley, New York, 1965).
- [3] G. Piccardi, Nature 124 (1929) 618; Atti. Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat. 21 (1935) 589; 25 (1937) 86.
- [4] S. Drapatz, L. Haser and K.W. Michel, Z. Naturforsch. 29a (1974) 411.
- [5] S.A. Edelstein, D.J. Eckstrom, B.E. Perry and S.W. Benson, J. Chem. Phys. 61 (1974) 4932.
- [6] D.J. Eckstrom, S.A. Edelstein, D.L. Huestis, B.E. Perry and S.W. Benson, Study of New Chemical Laser Systems, Semiannual Technical Report No. 1 (SRI MP74-40) Stanford Research Institute (August 30, 1974).
- [7] Ch. Ottinger and R.N. Zare, Chem. Phys. Letters 5 (1970) 243; C.D. Jonah, R.N. Zare and Ch. Ottinger, J. Chem. Phys. 56 (1972) 263; J.L. Gole and R.N. Zare, J. Chem. Phys. 57 (1972) 5331; R.C. Oldenberg, J.L. Gole and R.N. Zare, J. Chem. Phys. 60 (1974) 4032.
- [8] L.L. Ames, P.N. Walsh and D. White, J. Phys. Chem. 71 (1967) 2707.
- [9] K.F. Zmbov and J.L. Margrave, J. Inorg. Nucl. Chem. 29 (1967) 59.
- [10] R. Stair, W.E. Schneider and J.K. Jackson, Appl. Opt. 2 (1963) 1151.
- [11] (a) W.R. Savage, D.E. Hudson and F.H. Spedding, J. Chem. Phys. 30 (1959) 221; (b) O.C. Tulson, D.E. Hudson and F.H. Spedding, J. Chem. Phys. 35 (1961) 1018; (c) C.E. Habermann and A.H. Daane, J. Chem. Phys. 41 (1964) 2818.
- [12] P.J. Dagdigian, H.W. Cruse and R.N. Zare, J. Chem. Phys. March 1, 1975.
- [13] J.W. Edwards and P.A. Small, Nature 202 (1964) 1329; B.A. Thrush and J.J. Zwolenik, Trans. Faraday Soc. 59 (1963) 582.
- [14] W. Albertson, Phys. Rev. 47 (1935) 370.
- [15] A.L.G. Rees, J. Chem. Phys. 26 (1957) 1567.