# MOLECULAR BEAM CHEMILUMINESCENCE STUDIES OF THE SYSTEMS Sm–SF$_6$ AND Sm–CCl$_4$

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## Summary

The beam gas chemiluminescence reactions of samarium with SF$_6$ and samarium with CCl$_4$ have been studied. The emission is attributed to SmF$_2$* and SmCl$_2$* emitters. The reactions are first order with respect to both metal and oxidizer gas at low pressures. The total cross-section, chemiluminescence cross-section and photon yields for the reactions have been found to be 280 Å$^2$, 0.44 Å$^2$ and 0.0015 respectively for the samarium plus SF$_6$ reaction and 315 Å$^2$, 0.32 Å$^2$ and 0.001 for the samarium plus CCl$_4$ reaction.

## 1. Introduction

The reactions of samarium with the fluorine atom donors F$_2$ and NF$_3$ [1, 2] are amongst the most efficient chemiluminescence reactions with photon yields exceeding 50% per metal atom consumed at torr level pressures. The single-collision photon yields at much lower pressures are quite small (less than 1%) and comparable with other metal plus oxidant reactions. The large photon yields at high pressures are attributed to population of a large number of symmetry-allowed SmF product electronic states as a result of collision-assisted energy transfer processes. The observed chemiluminescence spectra are only slightly structured and no spectroscopic information on the spectra is available [3 - 5].

In this work we have chosen to study the reactions of samarium with other fluorine atom donors, the perfluoropolyatomic molecules SF$_6$, CF$_4$, C$_2$F$_6$ and C$_2$F$_4$, with a view to limiting the product electronic state accessibility as a result of the increased bond strength of the fluorine atom donor. While no visible emission was observed with the fluorocarbons as donor, the reaction between samarium and SF$_6$ gave chemiluminescence which is attributed to electronically excited samarium difluoride.

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Further, we compared the fluorine-based reaction with a chlorine-based reaction by studying the reaction of samarium with $CCl_4$, which had not previously been studied.

## 2. Experimental details

A molecular beam apparatus was built (Fig. 1) which consists of a differentially pumped two-compartment SS-304 vacuum chamber (inside diameter, 256 mm; height, 400 mm) [6].

The lower chamber houses a resistively heated metal beam oven supported on a removable bottom flange. The metal beam effuses through a 1 mm orifice and is further collimated by an adjustable $\phi$ 1 - 4 mm slit positioned on the partition plate between the two chambers which are differentially pumped by oil diffusion pumps at a rate of 500 l s$^{-1}$. The upper top plate supports a liquid nitrogen trap. The metal beam effuses vertically upwards and meets the oxidizer gas ($SF_6$, $CCl_4$, $CF_4$ etc.), that is fed through a 1 mm orifice. The absolute pressure at the source is measured using a Membranovac Mac-200 (Leybold–Heraus) absolute pressure gauge. The
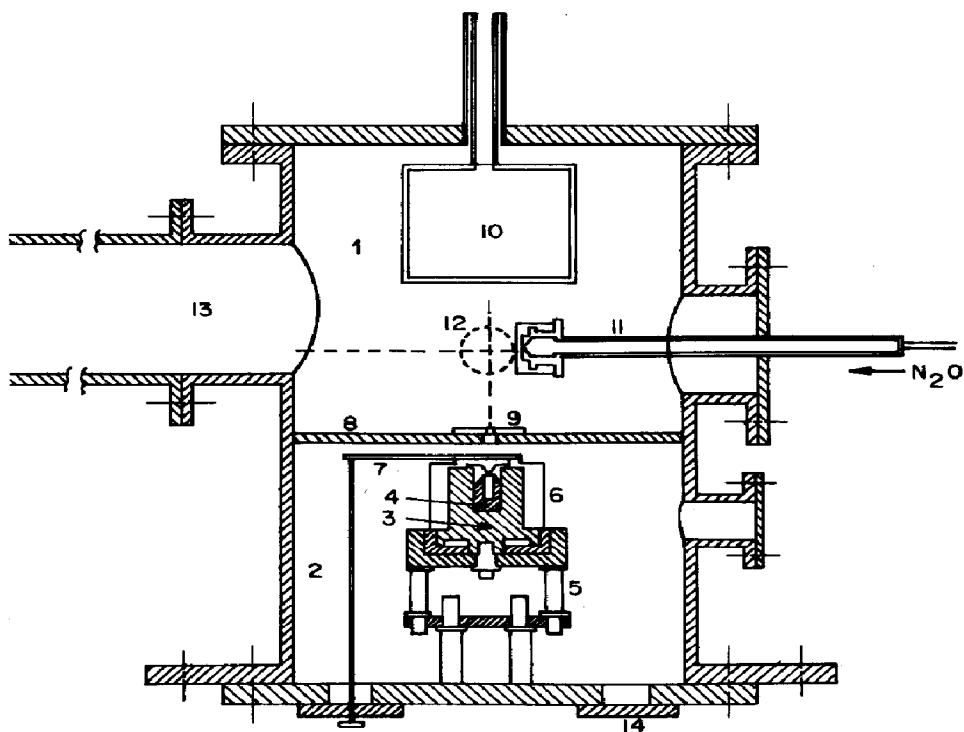


Fig. 1. Molecular beam chemiluminescence apparatus: 1, upper chamber; 2, lower chamber; 3, atomic beam oven (heater); 4, crucible; 5, atomic beam oven support; 6, heat shield; 7, beam flag; 8, partition plate; 9, collimator slit; 10, liquid nitrogen trap; 11, gas inlet (for molecular beam); 12, reaction zone; 13, port for oil diffusion pump.

chamber pressures were measured by means of a thermocouple and Penning gauges. The chemiluminescence generated in the reaction was monitored at right angles to the atomic beam, after collection by a lens (focal length, 5 cm) and then focused by another lens (focal length, 9 cm) on the slits of a Bausch and Lomb high intensity monochromator (typical resolution used, 3 nm) and detected by means of an EMI 9804 QB photomultiplier. (S-11 response gain, $2 \times 10^7$) and a Keithley 610B electrometer. To study the effect of an electric field on the chemiluminescence, a pair of ring electrodes was inserted across the metal beam (outside diameter, 18 mm; inside diameter, 12 mm; separation, 15 mm). As recommended by Zare and coworkers [3] the reaction between samarium and $N_2O$ was used as the standard reference reaction to calculate the cross-section.

## 3. Results

With $SF_6$ as the oxidant gas, a conical bluish green emission was observed from the entry point of the samarium beam into the scattering chamber. The observed flame was not diffuse, indicating that the emitting species have short lifetimes. With liquid nitrogen in the well in the top flange, the conical shape of the flame disappeared and the emission was confined to a small interaction zone defined by the dimensions of the atomic and molecular beams (diameters, 10 mm and 5 mm respectively).

Figure 2(a) shows the chemiluminescence spectrum for the reaction between samarium and $SF_6$ which extends from 325 to 600 nm with a peak at about 410 nm. The spectrum is uncorrected for the spectral response of the photomultiplier used which is insensitive beyond 600 nm.

No emission in the above wavelength region could be seen with the fluorocarbon gases $CF_4$, $C_2F_6$ and $C_2F_4$, even when the monochromator was removed and the photomultiplier was placed directly against the quartz window of the scattering chamber.

In contrast, $CCl_4$ reacted with samarium to give chemiluminescence, shown in Fig. 2(b), which is spectrally similar to the reported emission from $SmCl_2^*$, formed in the reaction between samarium and $Cl_2$.

No effect of an electric field on the chemiluminescence in the reaction between samarium and $SF_6$ was observed up to an applied potential gradient of 1100 V $cm^{-1}$.

### 3.1. Reaction kinetics: dependence of the chemiluminescence intensity I on the metal flux

Linear plots for $\ln(IT_b)$ against $1/T_b$, where $T_b$ is the metal oven temperature, were obtained for both samarium with $SF_6$ and samarium with $CCl_4$ (Fig. 3) at a fixed oxidant pressure showing that the reactions are first order with respect to the samarium flux. The slopes give values of $210 \pm 4$ kJ $mol^{-1}$ and $238 \pm 4$ kJ $mol^{-1}$ respectively for the two reactions. These values contain contributions from the heat of sublimation of the metal and the activation energy for the respective reaction.
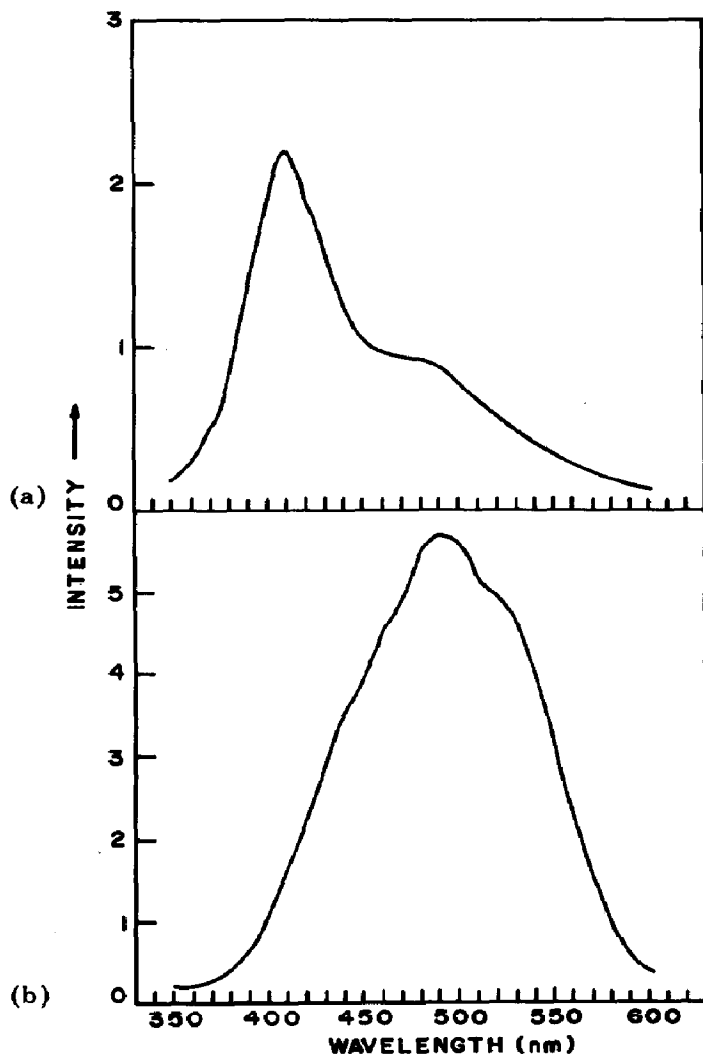
Fig. 2. Chemiluminescence spectra of (a) Sm + SF$_6$ (uncorrected) and (b) Sm + CCl$_4$ (uncorrected) (oven temperature, 1023 K; inlet SF$_6$ pressure, 0.8 Torr; inlet CCl$_4$ pressure, 0.6 Torr).

Using the method of Preuss and Gole [7, 8], we evaluated an activation energy of 34.7 ± 4 kJ mol$^{-1}$ for the reactions between samarium and CCl$_4$, taking the value reported in the literature for the heat of sublimation of samarium as 206.5 kJ mol$^{-1}$ [9].

### 3.2. Dependence of the chemiluminescence intensity I on the oxidant pressure for the system Sm–SF$_6$

A linear dependence of the chemiluminescence intensity on the SF$_6$ pressure at low oxidant pressures (10$^{-4}$ Torr or less) was observed, indicating that the excited product formation follows a simple bimolecular interaction
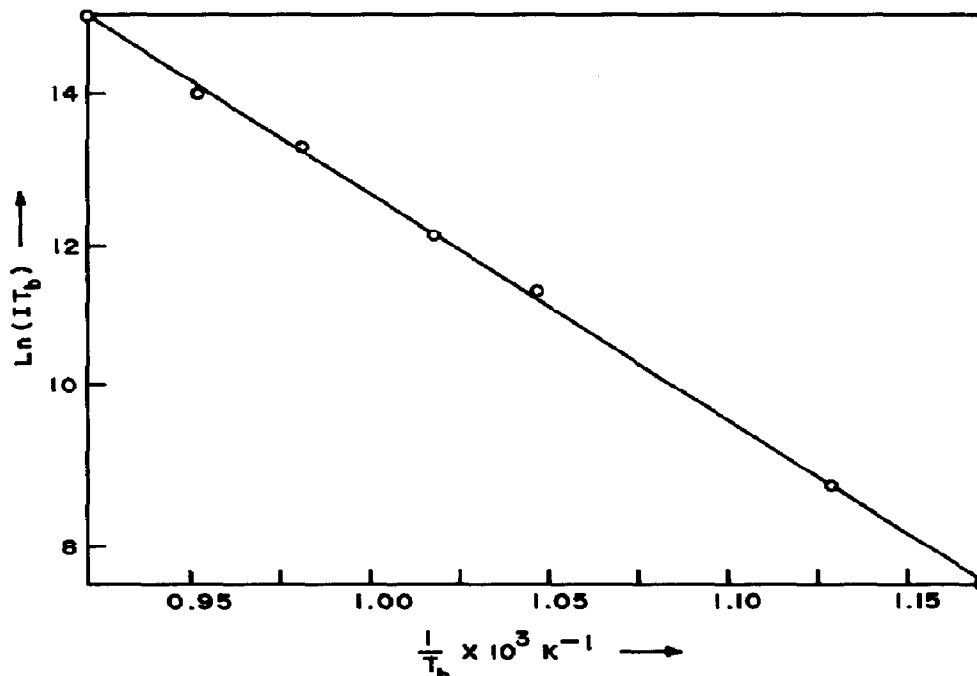
Fig. 3. Plot of ln($IT_b$) vs. $1/T_b$ (oven temperature) (inlet $CCl_4$ pressure, 0.6 Torr).

between samarium and $SF_6$. At higher $SF_6$ pressures, the attenuation of the samarium beam, as it reaches the viewing zone of the detector, introduces non-linearity in the plot of $I$ against $p(SF_6)$ (Fig. 4) and the curve obeys a $p \exp(-\alpha p)$ relationship (Fig. 5). The attenuation parameter $\alpha$ (Torr$^{-1}$) is related to the phenomenological cross-section $\sigma$ (Å$^2$) for the removal of samarium by the relation

$$\alpha = \frac{1.33 \times 10^{-13} \sigma l}{kT}$$

where $l$ is the path length of the samarium beam in the oxidizer gas (5.25 cm) up to the viewing zone, $k$ (erg K$^{-1}$) is the Boltzmann constant and $T$ is the temperature of the oxidant gas (300 K). The constant $1.33 \times 10^{-13}$ has units of dynes per torr per angstrom squared. The pressure at which the intensity is at its maximum is given by $\alpha = p_m^{-1}$. Since the response of the Penning gauge used for the pressure measurements in the scattering chamber is very much dependent on the oxidant gas used, it was estimated by comparison of the source pressure for the intensity maximum for the $SF_6$ reaction with that for the reaction between samarium and $N_2O$. From a known $\sigma$ value of 90 Å$^2$ for the Sm–$N_2O$ reaction, $\sigma = 280$ Å$^2$ was evaluated for the reaction between samarium and $SF_6$. The oxidant pressures in the scattering chamber mentioned in Fig. 5 are likewise obtained by cross-comparison of $\alpha$ with $p_{inlet, max}$.

Our value of $\sigma$ for Sm–$SF_6$ compares well with that reported by Dickson and Zare [5] for the Sm–$F_2$ reaction (304 Å$^2$).
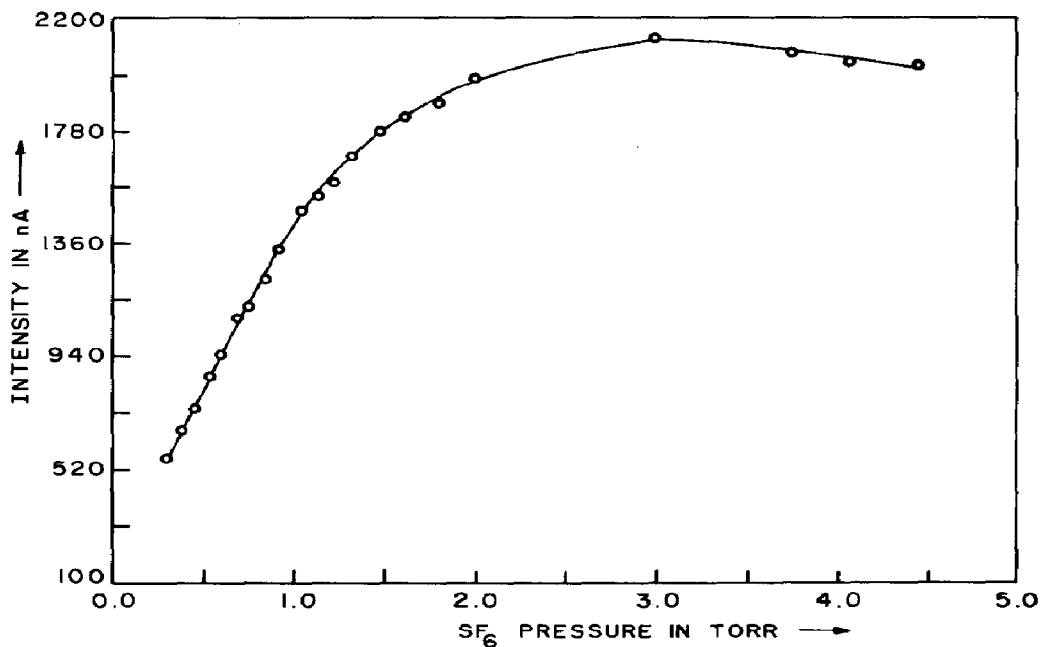
Fig. 4. Plot of chemiluminescence intensity $I$ vs. $SF_6$ pressure (oven temperature, 1023 K).
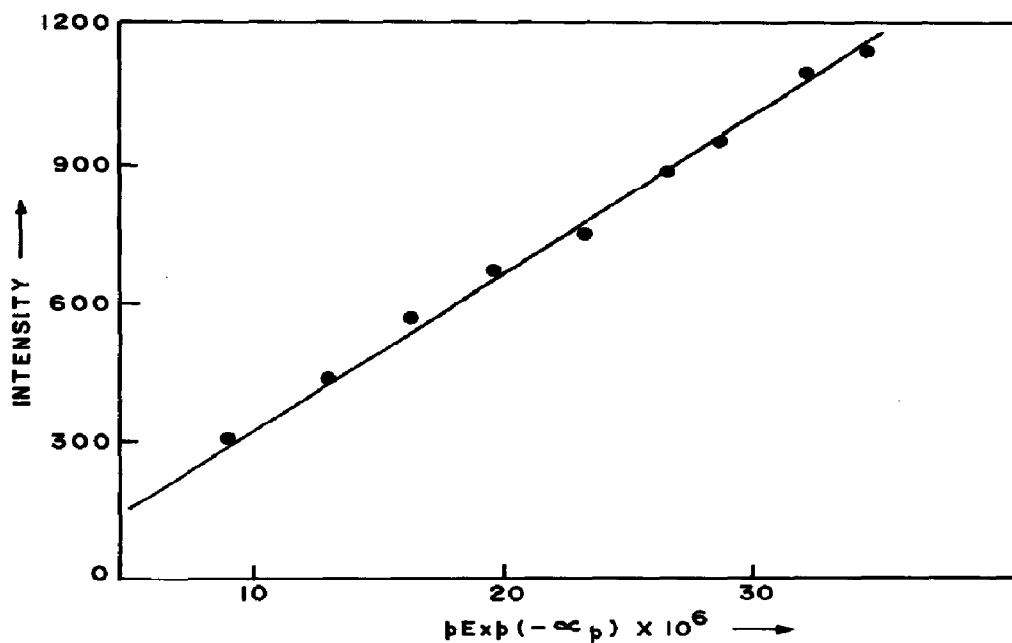


Fig. 5. Plot of chemiluminescence intensity $I$ vs. $p \exp(-\alpha p)$ (where $p$ is the $SF_6$ pressure) (oven temperature, 1023 K).

### 3.3. *The system Sm–CCl₄*

The emission intensity is also linearly dependent on $p$ at low $CCl_4$ pressures. In the extended range of pressures, the $I$ against $p$ curve obeys the $p \exp(-\alpha p)$ relationship. From the observed value of $p_m$, $\sigma = 315$ Å$^2$ was evaluated for this reaction.

### 3.4. *Photon yields*

The relative photon yield for the reaction between samarium and $SF_6$ is determined by comparison of the integrated emission intensities (corrected for the spectral response of the photomultiplier used) with those obtained for the reaction between samarium and $N_2O$. For the samarium plus $N_2O$ reaction, the emission intensity in the 350 - 600 nm wavelength range investigated is taken as $0.4I$ (350 - 800 nm). At constant metal flux, and the same pressure for the two oxidants, $N_2O$ and $SF_6$, the spectrally corrected intensity ratios are given by

$$\frac{I(SF_6)}{I(N_2O)} = \frac{\sigma(SF_6)\bar{V}(SF_6)}{\sigma(N_2O)\bar{V}(N_2O)} \exp\{-p(\alpha_{SF_6} - \alpha_{N_2O})\}$$

We evaluated the chemiluminescence cross-section $\sigma_{CL}$ for the reaction between samarium and $SF_6$ to be about 0.44 Å$^2$ in the observed wavelength range taking $\sigma(N_2O) = 0.35$ Å$^2$ for the samarium plus $N_2O$ reaction, and where $\bar{V}$ is the average relative velocity of the molecule ($SF_6$ or $N_2O$). The single-collision photon yield is then obtained as

$$\phi = \frac{\sigma_{CL}}{\sigma} = 0.0015 \text{ or } 0.15\%$$

It is to be emphasized that the indicated 0.15% value for the photon yield is for the observed high energy region (less than 600 nm) and, as a result of long wavelength emission undetected in this work, the overall photon yields can be larger.
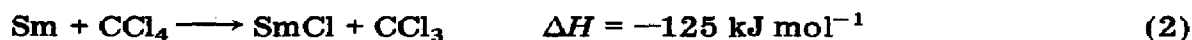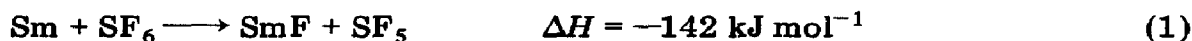
Similarly, for the samarium plus $CCl_4$ reaction $\sigma_{CL}$ is evaluated to be about 0.32 Å$^2$ and the photon yield about 0.1% in the observed spectral region.

## 4. Discussion

The above results clearly show that the observed chemiluminescence from both the Sm–$SF_6$ and Sm–$CCl_4$ reactions is produced by a single bimolecular encounter between the reactants in the pressure range studied. Secondary collisions involving an initial primary product and leading to either energy pooling or secondary product formation are ruled out as mechanisms for chemiluminescence since all such processes would show a quadratic dependence of the chemiluminescence intensity either on the metal atom concentration or on the pressure of the oxidant gas. This aspect was further assessed by carrying out a few beam–beam experiments and by
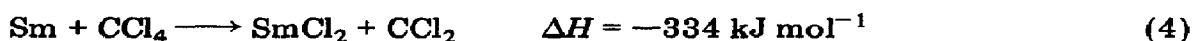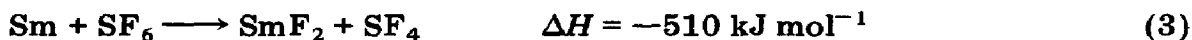
confirming a linear dependence of the chemiluminescence intensity on the $SF_6$ beam flux over an order-of-magnitude variation in its flux.

The chemiluminescent species produced in such single-collision reactions must necessarily have adequate internal energies to give rise to chemiluminescence spectra, which extend to 320 nm for the $Sm-SF_6$ reaction and to 360 nm for the $Sm-CCl_4$ reaction. When we take into account the known heats of formation and bond strengths for the reactants and products the initial internal energies of the reactants, the exoergicities for monohalide formation [10]

$$Sm + SF_6 \longrightarrow SmF + SF_5 \qquad \Delta H = -142 \text{ kJ mol}^{-1} \qquad (1)$$

$$Sm + CCl_4 \longrightarrow SmCl + CCl_3 \qquad \Delta H = -125 \text{ kJ mol}^{-1} \qquad (2)$$

are far too low to reach the chemiluminescence energies which are as high as 374 kJ mol$^{-1}$ and 333 kJ mol$^{-1}$ respectively. We therefore rule out monohalides as the chemiluminescent species on energetic grounds.

However, the dihalide formation is a very facile reaction with polyatomic halogen donors and takes place with large exoergicities [10]:

$$Sm + SF_6 \longrightarrow SmF_2 + SF_4 \qquad \Delta H = -510 \text{ kJ mol}^{-1} \qquad (3)$$

$$Sm + CCl_4 \longrightarrow SmCl_2 + CCl_2 \qquad \Delta H = -334 \text{ kJ mol}^{-1} \qquad (4)$$

The shortest discernible wavelengths for the chemiluminescence spectra of Fig. 2 are energetically within the reach of the above exoergicities. It is therefore concluded that $SmF_2^*$ and $SmCl_2^*$ are responsible for the present chemiluminescence.

The similarity of the chemiluminescence spectra observed for $SmCl_2^*$ with that reported from the samarium plus $Cl_2$ reaction further confirms a single-step mechanism for the dichloride formation in the present work. In the case of the halogen reaction, a two-step mechanism commensurate with the observed quadratic dependence of the spectral intensity on the chlorine pressure was suggested. Such a mechanistic difference is typical of metal atom reactions with elementary halogens and halogenated donors. The very large exothermicity released in associative reactions with halogens

$$M + X_2 \longrightarrow MX_2^{*, \neq} \qquad \Delta H > D_0^o(X-MX)$$

must be dissipated by secondary collisions before a bound dihalide can be stabilized. At the low pressures employed in the beam gas experiments, a dissociative reaction

$$MX_2^* \longrightarrow MX^* + X$$
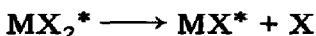
occurs more often than not and secondary steps

$$MX^* + X_2 \longrightarrow MX_2^* + X$$
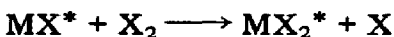
are more likely mechanisms for dihalide formation when elemental halogens are employed as reactants. In contrast, the availability of large internal states

for polyatomic reactants and products helps in energy disposal and primary product stabilization. Single-step difluoride formation was also recently reported by Rosano and Parson [11] in the reactions of tin, germanium and silicon with $SF_6$ and $SF_4$. In contrast, these Group IVA atom reactions with the free halogens $Br_2$ and $I_2$ take place by a two-step mechanism to give the respective dihalides.

The reaction energy distribution between two products is an important aspect of molecular dynamics. We have only limited information at present and the monitored chemiluminescence spectrum for $SmF_2^*$ suggests a $\lambda_{min}$ of about 320 nm, corresponding to 374 kJ $mol^{-1}$. The poor signal-to-noise ratio at shorter wavelengths prevents a clear-cut statement on whether or not the higher energy levels of SmF could be populated. If the observed limit is taken as the short wavelength cut-off, the dynamic channel leading to a separation of electronically excited $SmF_2^*$, e.g.

$$\left[ F_4S \overset{F}{\underset{F}{<\;\;>}} Sm \right]^* \longrightarrow SmF_2^* + SF_4$$
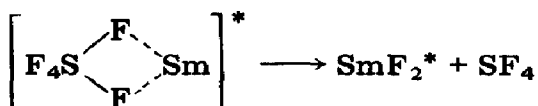
can leave behind a vibrationally excited $SF_4$ with an internal energy content as large as 134 kJ $mol^{-1}$, which corresponds to a vibrational temperature of 1800 K on a statistical basis.
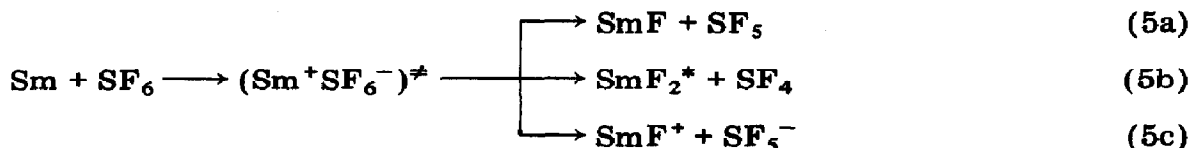
Considering the energy disposal a little further, we have two exoergic channels open for reaction except that the chemiluminescence channel is closed for monohalide elimination in the range studied. The lifetime of the polyatomic collision complex is determined by the internal energy available for disposal, the greater its magnitude the shorter its lifetime. With a simple RRK approximation one has

$$\tau^{-1} \propto \left( \frac{E - E^*}{E} \right)^{s-1}$$

where $E$ and $E^*$ are the internal energies available and fixed for a certain reaction channel. It is apparent that ground vibrational excitation $SmF_2(v)/SF_4(v)$ will occur preferentially. The electronic route locks up considerable energy as $E^*$ and any low-lying $SmF^*$ pathway ($\lambda > 800$ nm) would be nearly thermoneutral as far as the RRK complex is concerned, i.e. $E \approx 510$ kJ $mol^{-1}$, $E^* \approx 209$ - 376 kJ $mol^{-1}$ ($SmF_2^*$) and $E^* < E \approx 142$ kJ $mol^{-1}$ ($SmF^*$ elimination).

Although the single-collision chemiluminescence cross-sections are low, the reaction energy pool created by reaction (3) is larger than that for the reaction between samarium and $F_2$, i.e. about 510 kJ $mol^{-1}$ and about 376 kJ $mol^{-1}$ respectively. High pressure experiments in the samarium plus $F_2$ reaction have demonstrated very efficient energy pooling to the electronic state population. Similar up-pumping to the chemiluminescent states can possibly occur even with the $SF_6$ reaction although we have confined our present investigation to low pressure conditions.

The actual mechanism of the reaction and the nature of the collision complex cannot be completely assessed without a molecular beam experiment from which the angular distribution of products can be obtained. Ionic routes such as [12]

$$Sm + SF_6 \longrightarrow (Sm^+SF_6^-)^{\neq} \longrightarrow \begin{cases} \longrightarrow SmF + SF_5 & (5a) \\ \longrightarrow SmF_2^* + SF_4 & (5b) \\ \longrightarrow SmF^+ + SF_5^- & (5c) \end{cases}$$

are likely except that the endoergic barrier

$$IP(Sm) - EA(SF_6) \approx 5.6 - 1.51 = 4.09 \text{ eV}$$

where IP is the ionization potential and EA the electron affinity, for the electron transfer pair $Sm^+SF_6^-$ requires an interaction distance of about 3.5 Å for coulombic compensation, which is shorter than the mean scattering distance (about 9.6 Å). The mean scattering distance includes contributions from non-reactive scattering. Any such initial ion pair can become trapped in its coulombic potential well and in its extended life can transform itself into two electron transfer pairs, thus paving the way for cross-over to an electronic difluoride route. The absence of an electric field effect up to 1000 V cm$^{-1}$ rules out contributions to chemiluminescence from charge neutralization of any separated ionic products (eqn. (5c)).

## 5. Conclusions

The reaction of samarium with $SF_6$ and $CCl_4$ gives chemiluminescence attributable to samarium dihalide emitters. Reactions with oxidants having higher fluorine bond energies, *e.g.* $CF_4$, $C_2F_6$ and $C_2F_4$, do not give any emission in the region studied. Both the $SF_6$ and the $CCl_4$ reactions are first order with respect to both metal and oxidizer gas at low pressures. The total cross-section, chemiluminescence cross-section and photon yields for the reactions between samarium and $SF_6$ and samarium and $CCl_4$ were found to be respectively about 280 Å$^2$, about 0.44 Å$^2$ and about 0.0015 for the $SF_6$ reaction and about 315 Å$^2$, about 0.32 Å$^2$ and about 0.001 for the $CCl_4$ reaction using the reaction between samarium and $N_2O$ as a reference.

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