

MOLECULAR EMISSION SPECTRA IN THE VISIBLE AND NEAR IR PRODUCED IN THE CHEMILUMINESCENT REACTIONS OF MOLECULAR FLUORINE WITH ORGANOSULFUR COMPOUNDS

ROBERT J. GLINSKI^{a†}, ELIZABETH A. MISHALANIE^{b†} and JOHN W. BIRKS^b

^aNational Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307 (U.S.A.)

^bDepartment of Chemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309 (U.S.A.)

(Received May 7, 1986; in revised form July 29, 1986)

Summary

Rich chemiluminescence is observed in the gas phase reactions of F₂ with a variety of organosulfur compounds at room temperature and from 0.2 to 2.0 Torr. HCF(A¹A'') and vibrationally excited HF are observed in the reaction of F₂ with all the hydrogen-bearing compounds under varying conditions of reactant pressure. For the organosulfur reactants used in this study, CH₂S($\tilde{\alpha}$ ³A₂) is observed only with CH₃SH, CH₃SCH₃ and CH₃SSCH₃. The character of the emission spectra changes dramatically with changing reactant pressures or when CH₃OH or CH₃CN are present. CH₂S* is observed with CH₃CH₂SH and higher thiols when CH₃OH is present. A new vibrationally structured spectral feature appears ubiquitously in all of the reaction systems studied, and distinctly in the reaction of F₂ with CS₂. It is ascribed to an electronic transition of the transient species, FCS. The initiation of the reactions of F₂ with the stable organosulfur species and the implications of this work for IR multiphoton dissociation are discussed.

1. Introduction

The study of gas phase chemiluminescent reactions has often led to new spectroscopic data on interesting molecules and kinetic and mechanistic information on their formation. Ozone [1], halogens [2, 3], metal atoms and metal clusters [3 - 5] have been popular chemiluminescence reagents in the recent past. Atomic fluorine has been used as a chemiluminescence reagent in hydrogen abstraction reactions, where ground state HF vibrational

[†]Present address: Department of Chemistry, Tennessee Technological University, Cookeville, TN 38505, U.S.A.

[†]Present address: National Center for Atmospheric Research, Boulder, CO 80307, U.S.A.

distributions are of special interest in reaction dynamics [6]. Fluorine atoms have also been used to generate electronically excited molecular chemiluminescent products in reactions with halogen-containing, nitrogen-containing and organic compounds [7, 8]. Although molecular fluorine is frequently present in these reactions, its direct participation in the generation of the chemiluminescent products is usually neglected.

Reactions of molecular fluorine have, however, produced chemiluminescent products. Reactions of F_2 with other halogens [9, 10] and the hydrides of boron, silicon, germanium and nitrogen [11 - 14] have yielded vibrationally and electronically excited chemiluminescent products under high temperature flame conditions. It is often postulated that reactions of molecular fluorine are initiated by fluorine atoms that are in thermal equilibrium with molecular fluorine. Subsequent fluorine atom reactions are believed to be responsible for much of the chemiluminescence observed when F_2 is used as a reagent gas. As the reaction chain propagates and branches, heat builds up in the reaction mixture and the equilibrium favors atomic fluorine. Quasi-combustion conditions can then result in complex chemistry in the reaction mixture. The appearance of C_2^* and CH^* emission in the F_2 - CH_4 flame [14, 15] attests to the high degree of fragmentation of the fuel under these conditions.

To reduce the complexity of these reaction systems, the severe chemical conditions can be controlled in several ways. In the gas phase, fast pumping speeds and the presence of a buffer gas can keep the reactions close to room temperature. The arrested relaxation technique [6, 16] is an extreme example of this. The walls of the reaction vessel are maintained at cryogenic temperatures to trap every reactive product of the first reactive encounter between the reagents. The arrested relaxation experiments are also carried out at very low pressure to ensure single-collision conditions [6, 16]. Control of the reaction conditions can allow these reactions to be studied from few-collision conditions to many-collision or quasi-combustion conditions.

We have previously reported preliminary results of low pressure, room temperature reactions of F_2 with CH_3SH [17] and $(CH_3Se)_2$ [18] in the presence of a helium buffer gas. These studies yielded the phosphorescence spectra of CH_2S and CH_2Se . Vibrationally excited HF is also a major contributor to the emissions observed in the reactions of F_2 with a large number of organosulfur compounds [19]. Furthermore, it was reported that the chemiluminescence observed in the reactions of F_2 with organosulfur compounds was orders of magnitude more intense than that observed under the same conditions for the reactions of F_2 with other classes of compounds, *i.e.* oxygenated hydrocarbons, paraffins, olefins and nitrogen compounds [19]. This unique property has been exploited in the development of a sensitive and selective detector for organosulfur compounds in gas chromatography (GC) [19] and high performance liquid chromatography (HPLC) [20].

To investigate the relatively efficient chemiluminescent processes that occur in the F_2 -organosulfur compound reactions, we have made a detailed

survey of the emissions resulting from these reactions. We have obtained spectra of $\text{HCF}(\tilde{A}^1A'')$, $\text{CH}_2\text{S}(\tilde{a}^3A_2)$, and vibrationally excited HF from the reactions of F_2 with an array of organosulfur compounds at room temperature and total pressures ranging from 0.2 to 2.0 Torr. In addition, a recently discovered novel electronic spectrum, first identified during the reaction of F_2 with carbon disulfide and tentatively assigned to FCS [21], is observed frequently in the reactions of many organosulfur compounds. The reactions also were studied in the presence of large amounts of methanol and acetonitrile to characterize the chemiluminescence in the HPLC system.

2. Experimental details

The chemiluminescent reactions were studied in either a small volume reaction cell [19, 20] or a large volume, crossed effusive beam chamber [17]. A schematic diagram of the top view of the small volume (0.04 l), stainless steel reaction cell and spectrometer is given in Fig. 1. The construction of this cell for use as an analytical detector has been described in detail previously [20]. The emission resulting from the chemiluminescent reaction was viewed through two quartz windows of diameter 5 cm located on both sides of the reaction cell. On one side, the chemiluminescence was viewed by a cooled, red-sensitive photomultiplier tube (EMI, 9659QB). The PMT was operated when the reaction cell was used for HPLC or GC analyses [20]. The window opposite the PMT was used for spectroscopic investigations. An

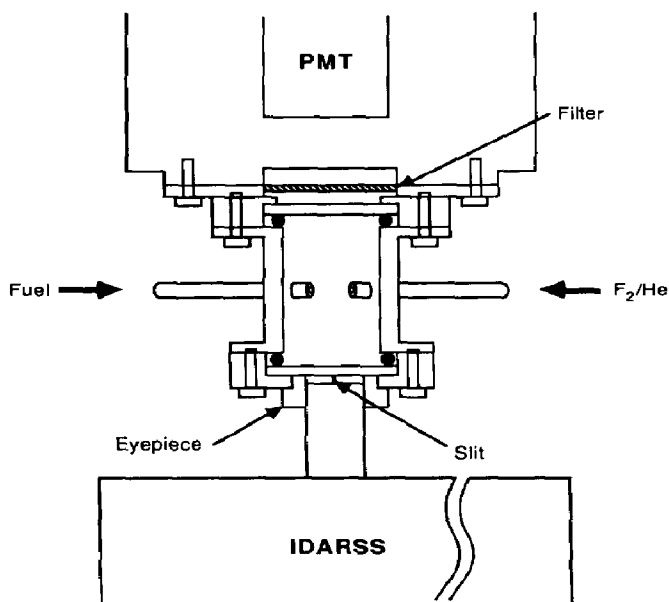


Fig. 1. Top view of the small-volume chemiluminescence chamber and IDARSS.

intensified diode array rapid scan spectrometer (IDARSS, Tracor Northern, TN1710) was positioned in front of the window. A 0.1 mm entrance slit was contained in an eyepiece attached to the front flange of the reaction cell. The spectrometer had a holographic grating of focal length 0.25 m and 512 diodes that spanned a 500 nm wavelength region.

Reactants were flowed into the pumped reaction cell through stainless steel tubing orthogonal to the cell axis and extending into the cell to about 1 cm from the crossing point. Pure organosulfur compound liquids were held in a Pyrex cold finger and introduced into the reaction cell by directly pumping on the liquid. The organosulfur reagent was introduced through a short length of 0.025 cm tubing. A 5vol.%F₂-95vol.%He or a 10vol.%F₂-90vol.%He reagent mixture was introduced through a 0.64 cm tube. The gas flow rates were controlled by needle valves.

To investigate the chemiluminescent reactions in the presence of vaporized methanol and acetonitrile, an HPLC pump, injector and vaporization line were utilized. A 2 ml sample loop was used to introduce a 10 - 20 vol.% organosulfur compound-90 - 80 vol.% solvent mixture into the 100 μl min⁻¹ HPLC solvent flow. All of the liquid reactant mixture was vaporized at 300 °C in the vaporization line before entering the reaction cell. Pure organosulfur reagents could also be introduced in this manner. The initial F₂-He pressure was 0.4 Torr. The addition of the volatilized reactants raised the pressure in the cell to about 0.9 Torr. The cell was evacuated by means of a dry-ice trapped mechanical pump, and the cell pressure was measured by a capacitance manometer.

The large-volume reaction cell was similar to the small cell illustrated in Fig. 1. The larger cell was a 12 cm aluminum cube. Effusive beam sources were formed by a 0.5 mm orifice in a KEL-F plug pressed into the end of a 0.25 mm stainless steel tube. The nozzles were 1.5 cm from the crossing point at the center of the cell. Only the diode array was used for optical detection. Pumping was accomplished in the same way as for the small chamber. Pure organosulfur compounds were introduced by directly pumping on a liquid in a cold finger.

The spectra were usually obtained by the following procedure. The signal was accumulated in a memory register of a multichannel analyzer for a time interval of 10 - 20 min with both reactants flowing. The organosulfur fuel flow was then turned off and the background signal was accumulated in another register for twice the initial time. The fuel was then turned back on and the signal accumulated in the original register for one time interval. The two registers were subtracted and the resulting spectrum was outputted to a chart recorder. The diode array was calibrated in wavelength by a low pressure helium line source. The spectra reported below were not corrected for the spectrometer response. (Although the spectra presented in this paper were not corrected for spectrometer response, the spectra can be normalized by using the following relative sensitivities of the IDARSS: 400 nm, 0.40; 450 nm, 0.80; 500 nm, 1.00; 550 nm, 1.00; 700 nm, 0.70; 850 nm, 0.25; 900 nm, 0.11.)

3. Results

3.1. Formation of vibrationally excited HF

Figure 2 shows a spectrum obtained from the reaction of 350 mTorr $\text{CH}_3\text{CH}_2\text{SH}$ with 3.5 Torr of a 5vol.% F_2 -95vol.%He mixture. The most intense features are the vibrational overtone emissions from ground state HF [22]. The only observable band in the $\Delta v = 3$ sequence is the 3-0 band. This is because of the greatly reduced response of the intensified diode array beyond 880 nm (see Section 2). The $\Delta v = 4$ sequence is complete to $v' = 8$. The $\Delta v = 5$ sequence appears weakly between 550 and 650 nm, and looks at first to be misassigned. The shapes of the features near the 7-2 and 8-3 transitions are inconsistent with the vibrational band contours of HF^\dagger . This inconsistency has been explained by the observation of emission bands between 600 and 650 nm in the reaction of F_2 with CS_2 . These bands, assigned to FCS as discussed below, can account for the interfering features near the 7-2 and 8-3 HF bands. Emission from $\text{HCF}(\tilde{A}^1A'')$ below 650 nm also appears weakly in the limit of low organosulfur concentrations, and is discussed below.

Spectra very similar to that shown in Fig. 2 are observed in the reactions of F_2 with all of the higher thiols, sulfides and disulfides. A summary of the chemiluminescent products observed in the reactions studied in this work is given in Table 1. The reactions can be grouped into two classes: the long-chain sulfides and thiols which produce primarily HF^\dagger , and the methyl-substituted species which produce $\text{CH}_2\text{S}(\tilde{a}^3A_2)$ and exhibit other complexities. In addition, the chemiluminescent product from the CS_2 - F_2 reaction [21] is often observed from 600 to 700 nm under fuel-lean conditions in spectra recorded during the reactions of F_2 with nearly all organosulfur species studied. This ubiquitous feature is discussed below for the $\text{CS}_2 + \text{F}_2$ system, where the spectrum occurs distinctly.

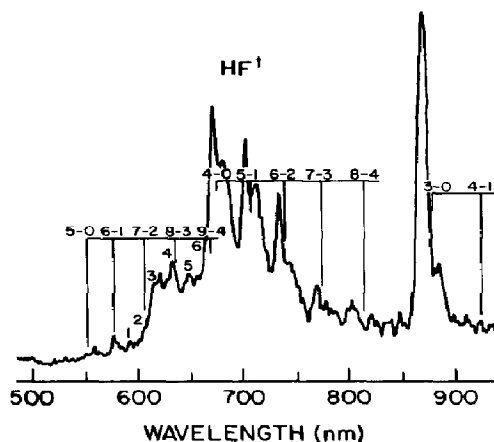


Fig. 2. Emission spectrum obtained in the reaction of $\text{CH}_3\text{CH}_2\text{SH}$ with the F_2 -He mixture. The HF vibrational overtone bands are marked. Features that can be ascribed to the FCS spectrum are numbered 1 through 6 (see Fig. 5).

TABLE 1

Observed emission features in the reactions of molecular fluorine with pure organosulfur species

| Reactant | Condition ^a | HF($\Delta v = 4$) ^b | HF(3-0) | CH ₂ S | HCF | FCS ^c |
|-----------------------------|------------------------|-----------------------------------|---------|----------------------|-----|------------------|
| MeSH | L | M | M | M | W | W |
| | H | W | W | S | | |
| Me ₂ S | L | W | M | W | S | W |
| | H | W | M | S | | |
| (MeS) ₂ | L | W | M | W | M | W |
| | H | W | M | S | | |
| Et ₂ S | H | M | S | | | W |
| Allyl ₂ S | L | M | S | | W | M |
| | H | M | S | | | |
| <i>t</i> -Bu ₂ S | H | M | W | | M | M |
| EtSH | L | M | M | | W | M |
| | H | S | S | | | W |
| OctSH | H | S | S | | | W |
| CS ₂ | H | | | | | M |
| CD ₃ SH | L | W | W | (CD ₂ S)M | | W |
| | H | W | W | (CD ₂ S)S | | |

^aL, low fuel; H, high fuel.

^bRelative intensity: S, strong; M, medium; W, weak.

^cTentative assignment (see text).

3.2. Formation of HCF* and CH₂S*

Figure 3 illustrates the effect of reactant concentration on the emitters formed in the reactions of (CH₃)₂S with molecular fluorine. The spectra obtained over a range of reaction conditions from fuel rich (Fig. 3(a)) to fuel lean (Fig. 3(c)) are given. Fuel-rich conditions are defined here as $P(\text{fuel}) > P(\text{F}_2)$. In other experiments, changes in the helium concentration comparable with the reactant concentration changes cited in Fig. 3 had little effect on the general features of the emission. Therefore, the reactant partial pressures were responsible for changes seen in Fig. 3 and not the total pressure. Figure 3(a) is very similar to spectra obtained during the reaction of F₂ with CH₃SH [17] and the features around 700 nm are assigned to thioformaldehyde (CH₂S) phosphorescence ($\tilde{a}^3A_2 \rightarrow \tilde{X}^1A_1$) with a minor contribution from HF($\Delta v = 4$). Figure 3(c) shows the intense appearance of the HCF($\tilde{A}^1A'' \rightarrow \tilde{X}^1A'$) spectrum under fuel-lean conditions. This HCF emission feature was first observed by Patel *et al.* [14] in the fuel-lean CH₄-F₂ flame, and is characterized by progressions in the HCF bending mode. The HF($\Delta v = 4$) bands are also observable in Fig. 3(c) around 700 nm, as well as a trace of the CH₂S($\tilde{a}^3A_2 \rightarrow \tilde{X}^1A_1$) feature.

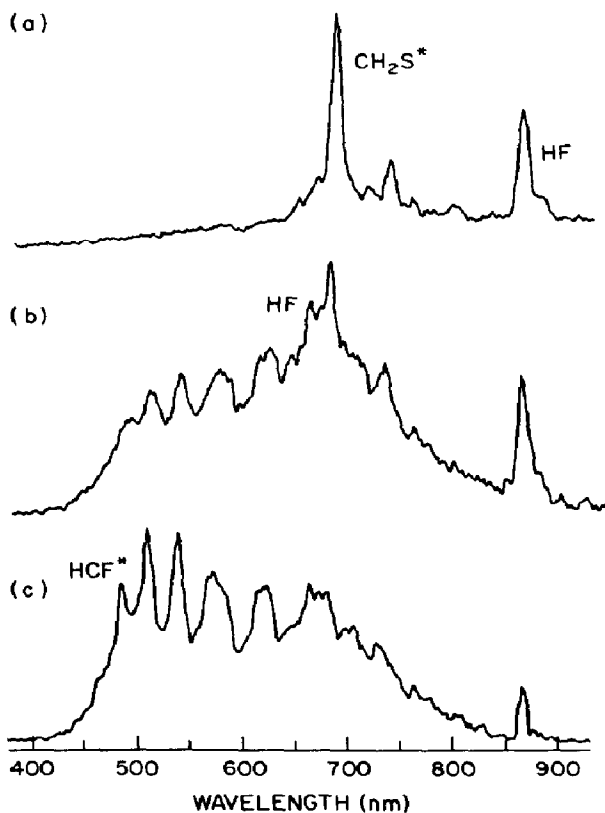


Fig. 3. Spectra illustrating the effect of reactant concentration on the emitters formed in the reaction of $(\text{CH}_3)_2\text{S}$ with molecular fluorine. (a) 155 mTorr CH_3SCH_3 , 30 mTorr F_2 , 570 mTorr He; (b) 30 mTorr CH_3SCH_3 , 20 mTorr F_2 , 350 mTorr He; (c) 30 mTorr CH_3SCH_3 , 50 mTorr F_2 , 900 mTorr He.

The HCF^* emission is most intense in the dimethyl sulfide system, although effects similar to those observed in Fig. 3 are observed in the methanethiol and dimethyl disulfide systems. The HCF^* feature is also much weaker in the higher thiol and sulfide spectra. No trace of thioformaldehyde phosphorescence is observed in the reactions of F_2 with the pure higher thiols and sulfides (*cf.* Table 1).

3.3. Spectral effects of solvent vapor

As described in the Section 2, the liquid organosulfur reactants were dissolved in either methanol or acetonitrile, and the mixture volatilized in a heated transfer line before entering the cell. Figure 4 shows the spectra obtained when ethanethiol is reacted with F_2 in the presence of methanol or acetonitrile vapor. When pure gaseous methanol or acetonitrile are reacted with F_2 , a very weak signal (many orders of magnitude less than when the organosulfur compounds are present) is observed by the PMT. The low light levels are insufficient for recording diode array spectra of the emissions from the pure solvent reactions.

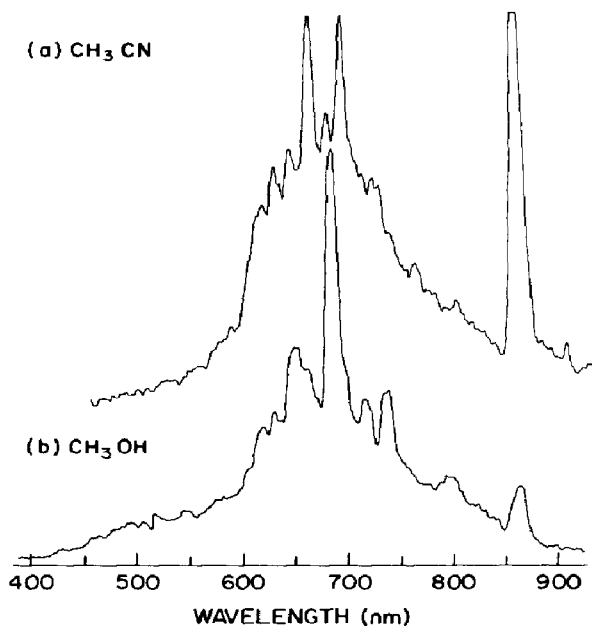


Fig. 4. Spectra obtained in the reactions of $\text{CH}_3\text{CH}_2\text{SH}$ with the Fe_2 -He mixture in the presence of (a) acetonitrile and (b) methanol. Spectrum (a) was obtained using a mixture of 20 vol.% ethanethiol in acetonitrile and spectrum (b) was obtained using a mixture of 10 vol.% ethanethiol in methanol.

Most of the emission in Fig. 4(a) is assigned to two different emitters. The most intense bands are from vibrationally excited HF. This spectrum can be compared with Fig. 2 where the HF features also occur. The 3-0 band of HF is obvious in Fig. 4(a) at 870 nm, and the two strongest bands of the $\Delta v = 4$ sequence are apparent at 670 and 700 nm. A broad, banded feature extending from 570 to 840 nm, thought to be the same as that observed in the CS_2 - F_2 system, is also observed in Fig. 4(a).

Spectrum 4(b) also exhibits the broad feature from 570 to 840 nm, but aside from this similarity the differences between spectra 4(b) and 4(a) are striking. The HF $\Delta v = 4$ bands are present in spectrum 4(b) but are considerably diminished compared with spectrum 4(a). Also, the HCF^* spectrum appears weakly in Fig. 4(b) to the blue of 600 nm, although some HCF^* may also appear weakly in Fig. 4(a). The reaction of ethanethiol with molecular fluorine in the presence of methanol yields intense emission from $\text{CH}_2\text{S}(\tilde{a}^3\text{A}_2)$. To determine whether the volatilization of the mixture in the heated transfer line affected these observations, we ran similar experiments with the transfer line temperature lowered to 120 °C. The reaction of F_2 with a 20vol.% octanethiol-80vol.% methanol mixture gave virtually the same spectrum, including the CH_2S^* feature, under these conditions as when the transfer line was at 300 °C.

Similar studies were carried out on a variety of organosulfur compounds. A summary of the results is presented in Table 2. These results can be compared with those of Table 1, and some general observations made:

TABLE 2

Observed gas phase emission features when the reactant is diluted in solvent

| <i>Reactant</i> | <i>Solvent</i> ^a | <i>HF</i> ($\Delta v = 4$) ^b | <i>HF</i> (3-0) | <i>CH</i> ₂ <i>S</i> | <i>HCF</i> | <i>FCS</i> ^c |
|-----------------------|-----------------------------|---|-----------------|---------------------------------|------------|-------------------------|
| Me ₂ S | M, 20 | W | W | S | W | |
| | M, 1 | W | W | S | M | |
| | A, 20 | M | M | S | W | |
| (MeS) ₂ | M, 10 | W | W | S | W | |
| | A, 10 | M | M | S | W | |
| Dimethyl sulfoxide | M, 40 | W | W | S | | |
| | A, 40 | W | M | S | | |
| Et ₂ S | M, 10 | M | W | | | S |
| | A, 10 | S | S | | | S |
| | H, 10 | M | M | | | M |
| Allyl ₂ S | M, 10 | M | M | | | S |
| | A, 10 | S | S | | | S |
| t-Bu ₂ S | M, 20 | M | W | | | S |
| Ph ₂ S | M, 20 | M | W | | | S |
| | A, 10 | M | W | | | S |
| EtSH | M, 10 | W | W | S | | M |
| | A, 20 | S | S | | | S |
| HexSH | M, 20 | W | W | S | | M |
| | A, 20 | S | S | | | S |
| OctSH | M, 20 | W | W | S | | M |
| | M, 20, 120 °C | W | W | S | | M |
| Thiophene | M, 20 | | | | | S |
| 1-Hexene | A, 40 | W | S | | | |
| CS ₂ | M, 20 | | | | | M |
| | A, 20 | | | | | M |

^aThe first entry means, for example, that a solution of 20% methyl sulfide in methanol by volume was vaporized at 300 °C. A, acetonitrile; H, hexane.

^bRelative intensity: S, strong; M, medium; W, weak.

^cTentative assignment (see text).

(a) the HF⁺ bands are diminished and the broad, banded feature somewhat enhanced when methanol is present in the reaction mixture, (b) acetonitrile has little effect on the HF features of all of the spectra and (c) thioformaldehyde phosphorescence appears intensely in spectra recorded during the reactions of the higher thiols with F₂ in the presence of methanol.

3.4. Formation of FCS*

The spectrum in Fig. 5 is essentially the same as that published previously [21]. The previous spectrum had better resolution and showed that

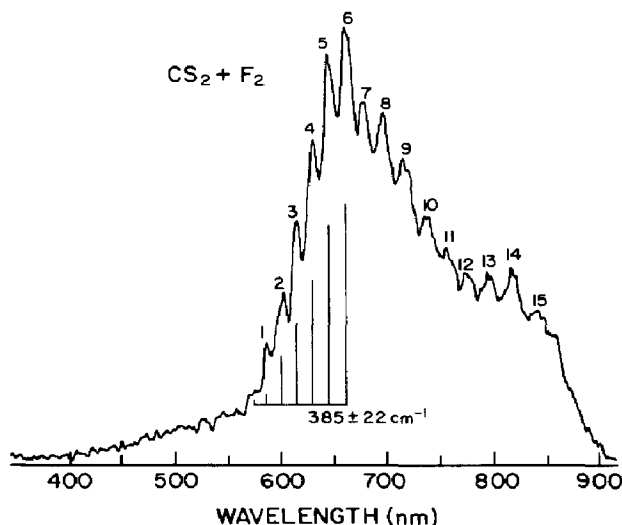


Fig. 5. Spectrum obtained in the reaction of 350 mTorr CS₂ with 75 mTorr F₂ and 1.4 Torr He. The numbering of the bands is arbitrary.

the bands labeled 1 - 15 in Fig. 5 resolve into vibrational bands that form long progressions of 356 and 831 cm⁻¹ [21]. The weak minimum near 750 nm observed in the spectrum in Fig. 5 was enhanced in other spectra obtained at higher CS₂ pressures. This was because of a relative increase in intensity of bands 13, 14 and 15. Correlated with the increased intensity of these bands, the weak continuum to the blue of 560 nm also increases relative to the most intense features. There is no trace of the HF 3-0 band at 870 nm. This implies that there is no significant amount of hydrogen-containing compounds in the reaction cell, *i.e.* reduced sulfur compounds or pump oil on the walls.

4. Discussion

Before discussing the emitting species and their formation, the nature of the bulk reaction mixture and the proposed initiation reactions will be described. Consider first the reaction mixture consisting of 100 mTorr of an organosulfur compound and 100 mTorr F₂ in 1 Torr He before any reactions occur. The F₂ ⇌ 2F· equilibrium constant is about 10⁻²⁰ atm at room temperature [23]. Thus, the fluorine atom concentration is only 10⁻⁸ of the F₂ concentration, or about 3 × 10⁷ F atoms cm⁻³. If the bi-molecular rate constant for the fluorine atom reaction with the fuel is assumed to be 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (this is the rate constant for one of the faster hydrogen-abstraction reactions of atomic fluorine; see ref. 16), then 9 × 10¹² reactions s⁻¹ cm⁻³ occur between fluorine atoms and the fuel. Now consider the reaction of molecular fluorine with the fuel. For this reaction to be as important as the reaction with fluorine atoms, the rate

constant for the reaction between the two molecular species must be only $10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

This is relatively slow and there is reason to suspect that F_2 will react faster with an organosulfur compound. A small amount of evidence exists suggesting that the reaction of molecular fluorine with alkenes occurs with non-zero rate [24]. The only reported rate constant for the homogeneous, gas phase reaction of F_2 with a stable molecular species is for the chemiluminescent reaction



The rate constant at room temperature is $1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. (A rate constant of $7.0 \times 10^{-13} \exp(-1150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is given for the reaction of F_2 with NO in the evaluation of Baulch *et al.* [25].) Therefore, the rate constant for the reaction of F_2 with organosulfur compounds could be greater than $10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

We also have assumed above that the $\text{F}_2 \rightleftharpoons 2\text{F}\cdot$ equilibrium is reached and maintained. This is a poor assumption since it neglects the rapid loss of fluorine atoms to the walls of the tubing on the way into the cell and that the equilibrium is then only very slowly regained in the cell. Hence, much fewer than $10^7 \text{ F atoms cm}^{-3}$ initially enter the cell. Therefore, we feel that reactions between F_2 and the sulfur fuel are more important than the reactions of F atoms in initiating the chemistry that results in chemiluminescence.

The reaction



may be considered to occur as the rate-limiting step that leads to chemiluminescence. A reaction similar to reaction (2) occurring between F_2 and an oxygen analog of the sulfide is expected to be much slower than the sulfide reaction. We observe that molecular fluorine does not react with the oxygenated hydrocarbons to give appreciable chemiluminescence under the same thermal conditions. This may explain the strong chemiluminescent reaction selectivity of the F_2 reactions with organosulfur compounds over paraffins and oxygenated hydrocarbons, since the rate of the rate-limiting step ultimately determines the chemiluminescence intensity.

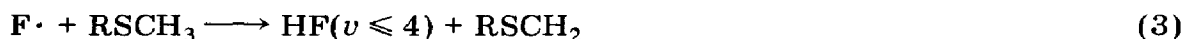
The average lifetime of a fluorine molecule in 100 mTorr of fuel is about 3 s. Since the residence time of the reactants in the cell is of the order of 0.1 s, only a small fraction of the reactants react in the cell. In addition, the buffer gas prohibits the reaction mixture from reaching an elevated temperature.

4.1. Formation of HF^\dagger

In a previous publication [19], a survey of the reactions of molecular fluorine with reduced sulfur compounds showed that ground state HF was produced in vibrationally excited states to as high as $v' = 6$. Included in the compounds studied were the higher sulfides, disulfides and thiols. Dimethyl

sulfide and dimethyl sulfoxide were also studied, and produced HF($v' = 6$) when reacted with molecular fluorine. No other emission features were reported for any of the reactions in that study [19]. In the present study, we have taken a more detailed look at the emission spectra employing varying reaction conditions and longer spectral integration times. The newly discovered complexity of these reaction systems is demonstrated by the results in Table 1. The general observation of vibrationally excited HF in the reactions of F₂ with the higher organosulfur compounds is, however, reaffirmed in Table 1.

Vibrationally excited HF is known to be produced in several types of chemical reactions that could be occurring in the F₂ reaction systems in this study. Fluorine atoms can abstract a hydrogen atom from reduced sulfur compounds to yield HF($v \leq 4$) [2, 26]:



It is probable that fluorine atoms are produced in the F₂ reaction system, which could account for some of the intensity in the HF 3-0 and 4-0 bands in accordance with reaction (3). In addition, since reactions such as

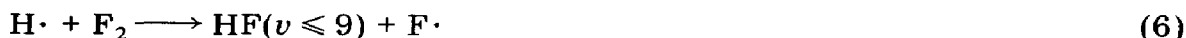


are exothermic ($-53 \text{ kcal mol}^{-1}$), translationally hot fluorine atoms could be formed, thereby increasing the exothermicity of reaction (3).

Other plausible pathways to HF($v \leq 8$) must also be considered, such as the attack of atomic fluorine on a reactive radical species:



Reactions of this kind, producing HF and a stable molecular species, would be highly exothermic. The rate of reaction (5), however, is expected to be relatively slow given the low concentration of the reactants [17]. Hydrogen atoms produce HF($v \leq 9$) on reaction with molecular fluorine [22]:



The observation of HF($v' = 8$) in Fig. 2 may indicate that hydrogen atoms are formed in the reactions of the present study.

4.2. Formation of HCF* and CH₂S*

The formation of HCF* in the reactions of fluorine with simple organic molecules in the gas phase is not unprecedented. The observation of HCF* in the CH₄-F₂ flame [14] suggests that the excited species may be formed in the reactions of F₂ with many hydrocarbon compounds when the initial activation barrier is overcome. The spectrum of HCF* has been investigated previously using the CH₄-F₂ flame [14], but the mechanism for its formation has not been discussed. Emissions from CH* and C₂* were also observed by Patel *et al.* [14] and Vanpee *et al.* [15] in the high temperature CH₄-F₂ flame. Emissions from these diatomic species were not observed under any conditions in the present study. Therefore, although the conditions under

which HCF* appears in this study allow many reactive collisions to occur, the inhibition of the chemistry by the buffer gas and the short residence time in the cell do not allow extensive combustion to occur.

The mechanism for the production of HCF* is probably the same in both systems, because the spectra obtained are essentially congruent. The shortest wavelength of emission, 480 nm, corresponds to an energy content of the HCF* product of 65 kcal mol⁻¹. Formation of HCF(\tilde{A}^1A'') with as much as five quanta in the bending mode (Fig. 3(c)) suggests that the reaction producing this species must be at least 65 kcal mol⁻¹ exothermic, and that the dynamics allow creation of the excited state species with a bond angle different than the equilibrium bond angle of the excited state.

Figure 3(a) shows a spectrum of thioformaldehyde phosphorescence. In a previous study [17], CD₃SH was employed to help assign the vibrational features and to help elucidate the mechanism of formation of HF⁺(DF⁺) and CH₂S*(CD₂S*). A short radical chain mechanism was proposed involving the CH₃S radical to account for the production of CH₂S*. The production of CH₂S* from dimethyl sulfide, dimethyl disulfide and methanethiol in the F₂-He system was thoroughly discussed previously [17], and will not be discussed in detail here.

4.3. Spectral effects of solvent vapor

The spectrum obtained during the reaction of molecular fluorine with ethanethiol in the presence of acetonitrile (Fig. 4(a)) may be compared with that of the ethanethiol-F₂ reaction in helium (Fig. 2). The HF⁺ features are evident in both figures. The most significant difference between the two spectra is that the banded emission feature is enhanced when acetonitrile is present. The spectrum of the ethanethiol-F₂-methanol reaction mixture (Fig. 4(b)) is considerably different from both Fig. 2 and Fig. 4(a). The banded feature is still relatively enhanced in Fig. 4(b) compared with Fig. 2. The HF⁺ bands in Fig. 4(b) are considerably diminished compared with those in Figs. 2 and 4(a). The appearance of CH₂S* in Fig. 4(b) is highly unexpected based on the results of the ethanethiol-F₂-He reaction system, and clearly demonstrates the participation of the solvent gas in the chemiluminescent reaction mechanism.

The solvent vapor may interact as a physical or chemical quencher in the reaction systems. Methanol can be considered to have physical quenching properties different from those of acetonitrile because of the potential for a hydrogen-bonding interaction between methanol and vibrationally excited HF [6, 27].

It is difficult to postulate a mechanism for the chemical quenching without knowledge of the identities of the reaction products or intermediates other than the chemiluminescent products. Methanol and acetonitrile can act as fluorine-atom scavengers, and this is probably initiated in the first steps of the reaction of molecular fluorine with the organosulfur compounds. Since methanol and acetonitrile are the reactants in excess by a

factor of as much as 5 - 10, their presence should make a large impact on the fluorine atom concentration and the entire radical chain chemistry.

4.4. Formation of FCS*

Based on spectroscopic and chromatographic information, it appears that the only elements present in the $\text{CS}_2\text{-F}_2$ reaction are sulfur, carbon and fluorine. No HF^+ was detected in the emission spectrum of this reaction (Fig. 5), which strongly suggests that there were no hydrogen-containing species in the reaction cell. This spectrum also was observed to some extent in every organosulfur compound- F_2 reaction studied including that with CD_3SH . Therefore, a logical assignment of the spectrum given in Fig. 5 is to a species having the general formula $\text{F}_x\text{C}_y\text{S}_z$. The spectroscopic evidence can be used to eliminate molecules that could not be the source of the emission band and to deduce the identity of the emitting species.

In a previous publication [21] a Deslandres table was constructed containing 36 bands that fit two progressions of unique frequencies. Arguments were also presented against the assignment of the new spectrum to other simple molecules, namely CF_2 , SF_2 , CS_2 and F_2CS . Based on the analogy with other XAB molecules the tentative assignment to FCS was made.

The assignment of FCS as the emitting species in Fig. 5 is strengthened by considering that the chemistry in these systems is compatible with the formation of FCS. Previous studies of two analogous reaction systems indicate this. The FCO radical has been studied by absorption spectroscopy both in the gas phase [28] and in a matrix [29]. In both cases, the molecule was formed by reacting fluorine atoms with CO. In the second reaction system, the three-body combination reaction of a fluorine atom with NO yielded the chemiluminescent product FNO [30]. It therefore may be that the reaction of a fluorine atom with CS forms FCS*.

4.5. Implications for IRMPD

These results may be useful in interpreting some of the new experimental data on the chemistry initiated by the IR multiphoton dissociation (IRMPD) of SF_6 . Spurlin and Yeung [31] have used IRMPD of SF_6 in the presence of hydrocarbons to obtain chemiluminescence from C_2 and CH. The results presented in the present study suggest that the conditions of the IRMPD system are much like those of the $\text{CH}_4\text{-F}_2$ flame of Vanpee *et al.* [15]. In addition, Pola *et al.* [32] have studied the stable products formed during the IRMPD of SF_6 in the presence of CS_2 . We suggest that the chemiluminescent system described in this paper may include chemistry similar to that of the system described by Pola *et al.* [32].

Acknowledgments

This work was supported by the Environmental Protection Agency, Grant No. R-810717-01-0. The National Center for Atmospheric Research is sponsored by the National Science Foundation, U.S.A.

References

- 1 S. Toby, *Chem. Rev.*, **8** (1984) 277.
- 2 B. Dill and H. Heydtmann, *Chem. Phys.*, **35** (1978) 161.
- 3 M. Menzinger, in K. P. Lawley (ed.), *Potential Energy Surfaces*, Wiley, New York, 1980, pp. 1 - 61.
- 4 R. W. Schwenz and J. M. Parson, *J. Chem. Phys.*, **76** (1982) 4439.
- 5 W. H. Crumley, J. L. Gole and D. A. Dixon, *J. Chem. Phys.*, **76** (1982) 6439.
J. R. Gole, R. Woodward, J. S. Haydon and D. A. Dixon, *J. Phys. Chem.*, **89** (1985) 4905.
- 6 M. A. Wickramaaratchi, D. W. Setser, H. Hildebrandt, B. Korbitzer and H. Heydtmann, *Chem. Phys.*, **94** (1985) 109.
B. S. Agrawalla and D. W. Setser, *J. Phys. Chem.*, **88** (1984) 657.
- 7 G. Schatz and M. Kaufman, *J. Phys. Chem.*, **76** (1972) 3586.
- 8 W. E. Jones and E. G. Skolnik, *Chem. Rev.*, **76** (1976) 563.
- 9 J. W. Birks, S. D. Gabelnick and H. S. Johnston, *J. Mol. Spectrosc.*, **57** (1975) 23.
- 10 R. H. Getty and J. W. Birks, *Anal. Lett.*, **12** (1979) 469.
- 11 C. P. Conner, G. W. Stewart, D. M. Lindsay and J. L. Gole, *J. Am. Chem. Soc.*, **99** (1977) 2540.
- 12 R. I. Patel and G. W. Stewart, *Can. J. Phys.*, **55** (1977) 1518.
- 13 D. M. Lindsay, J. L. Gole and J. R. Lombardi, *Chem. Phys.*, **37** (1979) 333.
- 14 R. I. Patel, G. W. Stewart, K. Casleton, J. L. Gole and J. R. Lombardi, *Chem. Phys.*, **52** (1980) 461.
- 15 M. Vanpee, K. D. Cashin and R. J. Mainiero, *Combust. Flame*, **31** (1978) 187.
- 16 D. J. Smith, D. W. Setser, K. C. Kim and D. J. Bogan, *J. Phys. Chem.*, **81** (1977) 898.
- 17 R. J. Glinski, J. Nelson Getty and J. W. Birks, *Chem. Phys. Lett.*, **117** (1985) 359.
- 18 R. J. Glinski, E. A. Mishalanie and J. W. Birks, *J. Am. Chem. Soc.*, **108** (1986) 531.
- 19 J. K. Nelson, R. H. Getty and J. W. Birks, *Anal. Chem.*, **55** (1983) 1767.
J. K. Nelson, *Ph.D. Thesis*, University of Colorado, 1984.
- 20 E. A. Mishalanie and J. W. Birks, *Anal. Chem.*, **58** (1986) 918.
E. A. Mishalanie, *Ph.D. Thesis*, University of Colorado, 1985.
- 21 R. J. Glinski, *Chem. Phys. Lett.*, **129** (1986) 342.
- 22 D. E. Mann, B. A. Thrush, D. R. Lide, Jr., J. J. Ball and N. Acquista, *J. Chem. Phys.*, **34** (1961) 420.
- 23 B. Lewis and G. von Elbe, *Combustion, Flames, and Explosions of Gases*, Academic Press, New York, 1961, p. 681.
- 24 W. T. Miller, Jr., and S. D. Kock, Jr., *J. Am. Chem. Soc.*, **79** (1957) 3084.
W. T. Miller, Jr., and A. L. Dittman, *J. Am. Chem. Soc.*, **78** (1956) 2793.
J. M. Tedder, in M. Stacey, J. C. Tatlow and A. G. Sharpe (eds.), *Advances in Fluorine Chemistry*, Vol. 2, Butterworths, Washington, DC, 1961, pp. 104 - 137.
S. Shobatake, J. M. Parson, Y. T. Lee and S. A. Rice, *J. Chem. Phys.*, **59** (1973) 1416.
- 25 D. L. Baulch, S. J. Grant, J. Duxbury and D. C. Montague, *J. Phys. Chem. Ref. Data*, **10** (1981) Supplement 1.
- 26 W. H. Duewer and D. W. Setser, *J. Chem. Phys.*, **58** (1973) 2310.
- 27 P. R. Poole and I. W. M. Smith, *J. Chem. Soc. Faraday Trans. 2*, **73** (1977) 1447.
J. K. Hancock and W. H. Green, *J. Chem. Phys.*, **57** (1972) 4515.
- 28 D. K. W. Wang and W. E. Jones, *J. Photochem.*, **1** (1972) 147.
- 29 M. E. Jacox, *J. Mol. Spectrosc.*, **80** (1980) 257.
D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford and D. E. Mann, *J. Chem. Phys.*, **42** (1965) 3187.
- 30 E. G. Skolnik, S. W. Veysey, M. G. Ahmed and W. E. Jones, *Can. J. Chem.*, **53** (1975) 3188.
H. S. Johnston and H. J. Bertin, Jr., *J. Mol. Spectrosc.*, **3** (1959) 683.
- 31 S. R. Spurlin and E. S. Yeung, *Anal. Chem.*, **57** (1985) 1223.
- 32 J. Pola, M. Horak and P. Engst, *J. Fluorine Chem.*, **18** (1981) 37.
J. Pola, *Collec. Czech. Chem. Commun.*, **47** (1982) 918.