

HF Fluorescence and Ion Production From Infrared Laser Irradiation of SF₆-Hydrocarbon Mixtures

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CO₂ laser irradiation of SF₆/hydrocarbon mixtures are shown to produce positive ions and infrared fluorescence due to emission by HF⁺. The mechanism for the production of these ions and fluorescence involves the multiple photon dissociation of SF₆ and subsequent attack of the free fluorine atom on the hydrocarbon, as well as *V* → *V* transfer and thermal ionization reactions. Argon and oxygen are found to increase ion production while quenching the fluorescence. Chemi-ionization of the hydrocarbons by a reaction sequence initiated by the attack of fluorine atoms on trace amounts of an oxygen impurity cannot be disregarded as a channel for ion formation.

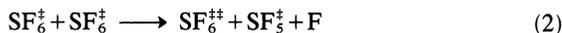
INTRODUCTION

Intense irradiation of SF₆ and hydrocarbon mixtures by a pulsed CO₂ laser tuned to the SF₆ absorption band has been shown to give rise to visible chemiluminescence from CH and C₂ species,¹ and under appropriate experimental conditions to lead to production of ions as well.² The first step in the proposed mechanism for the production of these ions is infrared multiple photon dissociation of SF₆ to produce free fluorine atoms,³



where the ‡ signifies a vibrationally excited species. Free fluorine

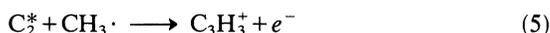
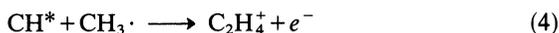
can also be produced by collisional dissociation of vibrationally hot SF_6 .⁴



Once a fluorine atom is produced, it can abstract a hydrogen atom from the hydrocarbon in a very fast exothermic reaction such as (3)⁵



in which methane is a representative example. The hydrogen fluoride generated is vibrationally excited and will relax slowly in the absence of collisions.^{6,7} The state of the methyl radical is not known. Successive hydrogen abstraction from the hydrocarbon by the fluorine atom can produce radical species which, if highly excited, can lead to ion formation through radical-radical recombination^{2,8} as shown by reactions (4) and (5).



The * denotes an electronically excited state.

We have investigated ion-producing reactions of SF_6 with small hydrocarbons such as methane and present evidence that the initial reaction steps in the mechanism of ion formation follow the reaction sequence proposed by Crim *et al.*² This path is valid only for saturated hydrocarbons. Reactions of atomic fluorine with small unsaturated molecules such as ethylene proceed by different routes, to be discussed later. Our observations are as follows. Firstly infrared luminescence from the vibrationally excited HF produced in reactions such as (3) is observed in the initial decomposition step. Secondly, atomic fluorine scavengers such as H_2 , CO and the nitrogen oxides are found to inhibit ion production, presumably by quenching reaction (3) before attack on the hydrocarbon can take place. Thirdly, when D_2 is used as an atomic fluorine scavenger instead of H_2 ion production decreases as does the HF^{\ddagger} infrared fluorescence with increased D_2 partial pressure. This is accompanied by increased infrared fluorescence in the region $2000\text{--}3200\text{ cm}^{-1}$, which is attributed to DF^{\ddagger} . In addition we see evidence for the presence of competing $V \rightarrow V$ transfer between SF_6 and CH_4 due to the observation of ion signal under conditions where enough scavenger is added to fully titrate all the fluorine atoms.

EXPERIMENTAL

A diagram of the experimental apparatus is shown in Figure 1. A line-tuned Lumonics 801 TEA CO₂ laser, operating in the TEM₀₀ mode, is used to generate up to 0.18 J/pulse of infrared energy, depending on the wavelength. The pulse is attenuated by means of a propylene filled glass cell with ZnSe windows. The laser is operated at 10 Hz with a typical pulse-width of 200 ns full-width at half-maximum on the P(24) line of the 10.6 μm band. The beam is focused by a 20 cm BaF₂ lens into a stainless steel cell to which KCl windows are mounted with viton O-ring seals. Energy deposition is measured by a Gen Tec energy meter placed behind the cell. Ions are collected by three independent parallel sets of 2 cm × 2 cm copper plates. This configuration makes independent biasing and ion collection possible. The time dependent ion signal is displayed on an oscilloscope. Typically, a 75 volt collection potential is impressed across each set of plates. Increasing the bias on the plates above 75 volts reduces the drift time of the ions from the production zone to the plate and causes

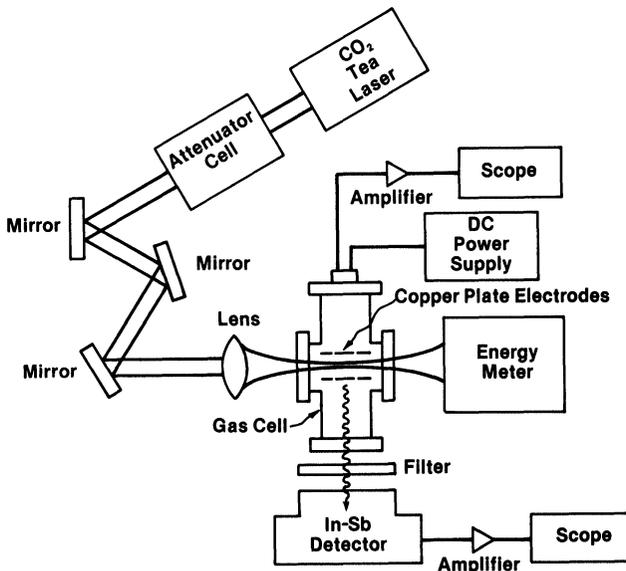


FIGURE 1 Schematic of the experimental apparatus.

the time between the laser pulse and the peak of the ion signal to decrease. Decreasing the bias below 75 volts had no observable effect on the signal down to 50 volts below which a decrease in signal intensity is observed down to the point of zero applied potential. This may be due to the loss of gain or ion recombination due to lower drift time. Reversing the bias results in a negative signal comparable in intensity and temporal behavior to that of the positive voltage, indicative of negative ion collection. Changing the bias has no effect on the HF fluorescence.

The focusing lens and cell are positioned so that the maximum ion current is collected on the center plate, with lower but equivalent ion current being collected on the plates on either side of it. This is due to the "dogbone" geometry of the focused CO₂ laser beam, which has maximum fluence at the center plates, with equal but lower fluence on either side of this focus.

HF fluorescence is observed by a 77 K InSb detector positioned at a right angle to the laser beam. A sapphire window allows infrared luminescence above 2000 cm⁻¹ to pass out of the cell, and a band pass filter isolates the 3200–5000 cm⁻¹ region, which includes emission from the three lowest vibrational bands of HF.

Reactants are fed into the cell via a gas manifold and pressures are monitored by an MKS Baratron capacitance manometer mounted directly to it. All gases were UHP grade or better and were used as received.

RESULTS

Figure 2 shows the time dependence of the ion current signal and HF fluorescence for a 50:50 mixture of SF₆/CH₄ (2 torr total) at an irradiation energy of 80 mJ/pulse, 10 Hz repetition rate. This ion signal, when measured with an electrometer, gave an average current with an order of magnitude of 10⁻¹² amperes. The ion current increased quadratically with laser fluence while the HF fluorescence increased with fluence as the 1.5 power. When the CO₂ laser was tuned to transitions outside the absorption band of SF₆ no ion signal or HF fluorescence was observed. With pure SF₆ neither ions nor IR emission was observed. It was noted that, with a fresh fill of SF₆ a transient ion signal, which disappeared after a few laser pulses was

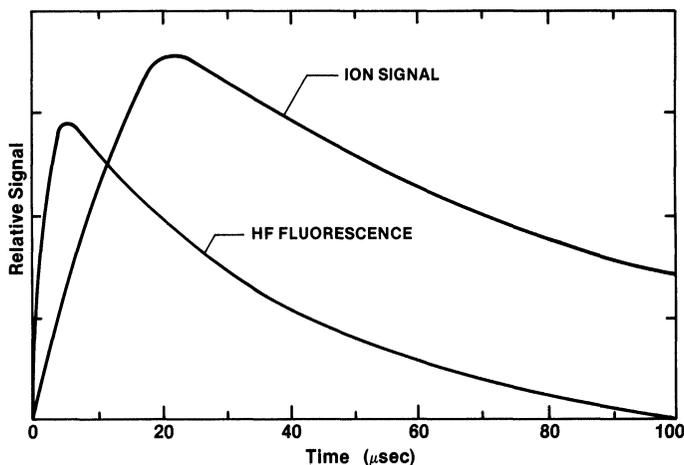


FIGURE 2 Ion signal and HF fluorescence from 1 torr each SF_6/CH_4 . $P_{\text{total}} = 2$ torr. Laser energy = 80 mJ/pulse.

observed. No ions or HF fluorescence could be observed with the hydrocarbons alone. Adding 5 torr of argon to the 1 torr $\text{SF}_6/1$ torr CH_4 mixture increased the magnitude of the ion signal from 0.18 V to 4 V but also shifted the peak of the ion signal later in time. Similar results were observed when diatomic oxygen was substituted for argon. The shift in ion peak to longer times is attributed to slower drift velocity of ions to the collection plate electrode due to the larger number of collisions at the higher total pressure. Applying a higher collection voltage increases the ion drift velocity and can return the ion peak to the original time if desired. Addition of up to 2 torr H_2 to 1 torr each of CH_4 and SF_6 caused both ion signal and IR emission to decrease with laser irradiation time until no ion signal was seen. When ions are no longer detected the HF fluorescence temporal behavior closely resembles that observed from SF_6/H_2 mixtures at comparable pressures.^{8,10} Similar behavior was observed when deuterium was substituted for hydrogen. Although no IR luminescence measurements were done under conditions where CO , NO , N_2O or NO_2 were added as scavengers to the mixture, a decrease in ion signal was observed and is attributed to scavenging of atomic fluorine. Figure 3 shows the ion signal intensity versus time at 10 torr added pressure for various fluorine atom scavengers. At comparable

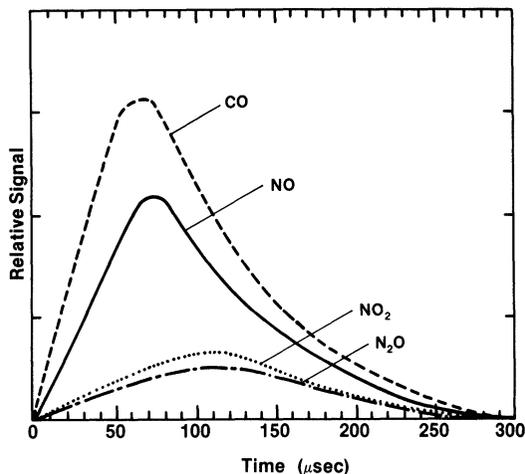


FIGURE 3 Ion signal of 1 torr each SF_6/CH_4 with 10 torr scavenger added to the mixture. $P_{\text{total}} = 12$ torr. Laser energy = 80 mJ/pulse.

pressures, the absorbed energy was essentially constant for the various scavengers. If the CH_4 pressure is reduced below 1 torr, the ion signal and HF fluorescence disappear with irradiation time. This is illustrated by Figures 4 and 5 where peak ion signal and peak fluorescence intensity are plotted versus time, represented by number of laser pulses. The ion signal behavior is exponential while the disappearance of the fluorescence signal is close to linear. Blocking and then unblocking the laser beam during the course of the reaction results in the same values of ion signal and HF^+ fluorescence as those seen just before the beam was blocked. Such experiments show that the phenomenon we are observing is dependent on the laser and that no appreciable concentration of reactive intermediate is present after the laser pulse to propagate the reaction.

Other experiments were performed in which the total pressure was kept constant in order to keep the number of collisions between molecules approximately constant. This was done by adding a certain pressure of scavenger to the 2 torr SF_6/CH_4 and balancing the total pressure to 12 torr with either argon or oxygen. Table I shows the ion current behavior of various Ar/ NO_2 mixtures as a function of

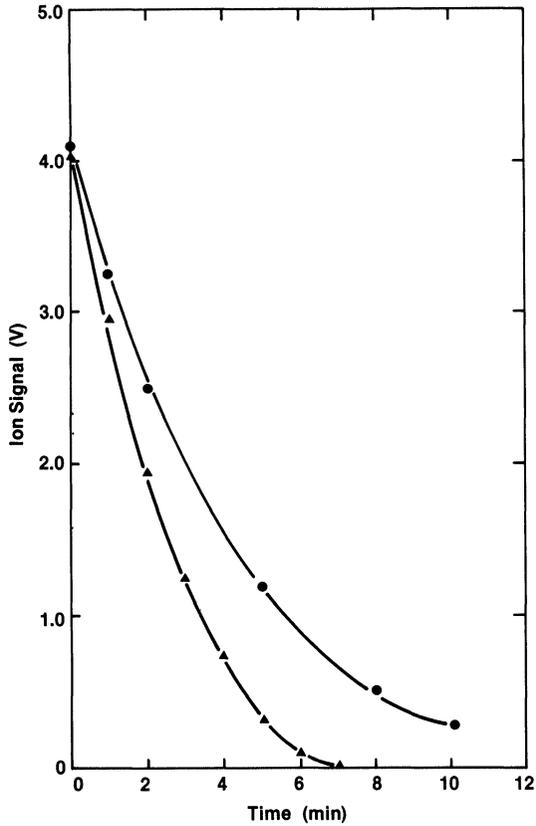


FIGURE 4 Ion signal intensity versus time for 1 torr SF_6 with 0.5 torr CH_4 (●) and 0.5 torr $\text{CH}_4/0.5$ torr H_2 (▲).

TABLE I
Ion signal peak height for 1 torr each SF_6/CH_4 versus pressure ratio of NO_2/Ar

P_{NO_2} (torr)	P_{Ar} (torr)	Ion peak height (volts)
0	10	4.7 ± 0.1
1	9	3.9 ± 0.1
5	5	0.560 ± 0.010
9	1	0.290 ± 0.005
10	0	0.250 ± 0.005

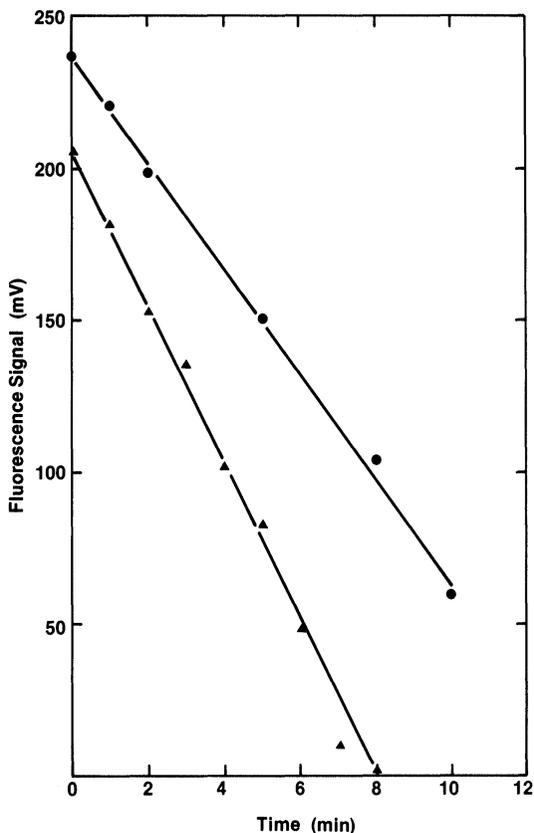


FIGURE 5 HF fluorescence intensity versus time for 1 torr SF_6 with 0.5 torr CH_4 (●) and 0.5 torr $\text{CH}_4/0.5$ torr H_2 (▲).

the relative NO_2 pressure. Note that the ion signal drops by a factor of 20 as the NO_2 pressure is increased to 10 torr. Other scavengers (NO , N_2O , CO) gave qualitatively similar results. Although most of our experiments involve using methane as the hydrocarbon probe, some investigations of ethylene and ethane under comparable conditions were done. Relative to methane, ethane showed only a very slight ion signal but comparable HF fluorescence; ethylene showed no ion current and less HF emission.

DISCUSSION

These results suggest that under our experimental conditions the first step in the proposed mechanism is dissociation of SF₆ by multiple photon absorption of infrared photons. The observations of HF luminescence and positive ion currents are consistent with the hypothesis of Crim and co-workers, who postulated that multiple photon dissociation of SF₆ occurs first, followed by exothermic reaction of the fluorine atoms with hydrocarbons to form HF and free-radicals which subsequently undergo chemi-ionization if energetically allowed. Those authors tabulated a partial list of allowed energetics for CH and C₂ radicals which presumably are involved here.²

The rate constant for the abstraction reaction of hydrogen from methane by free fluorine has been measured in a fast flow reactor system with mass spectrometric detection to be $3.3 \times 10^{14} \exp(-1150/RT) \text{ cm}^3\text{-mol}^{-1}\text{-s}^{-1}$.⁹ Similar values of this rate constant obtained by different methods are well documented.¹⁰ Under our experimental conditions, the rate of HF⁺ formation is $1.8 \times 10^7 \text{ s}^{-1}$. This rate constant is sufficiently large that one would expect HF to be formed within a few microseconds with subsequent ion reactions occurring later in time. The fluorescence signal reaches a maximum in $<10 \mu\text{s}$, while the ion signal does not reach its maximum until approximately $20 \mu\text{s}$ later. Both fluorescence and ion signal follow single exponential behavior, with $t_{1/2}$ lifetimes of 25 and 50 μs respectively. Simultaneous measurements of HF fluorescence and ion signal are limited by the fact that the diagnostics monitor different reaction channels. The HF fluorescence is a direct measure of the first and second steps of the reaction mechanism, SF₆ dissociation and alkyl radical formation by atomic fluorine attack on the saturated hydrocarbon, respectively. On the other hand, the ion current is an integrated measure of the chemistry occurring following radical formation. The results shown in Figure 2 support this claim. No corrections have been made for ion drift time, which are necessary to directly probe the different ion chemistry channels, i.e., what ions are produced. Experiments with a mass spectrometric probe to identify the ions produced in the various stages of this process are now under design.

From beam profile measurements, we estimate an irradiation volume of $1.5 \times 10^{-2} \text{ cm}^3$. At pressures of 1 torr each SF₆ and CH₄

a maximum of 5.0×10^{14} SF_6 molecules can be dissociated,¹¹ assuming 100% SF_6 dissociation yield, which means that there would be at least 5.0×10^{14} fluorine atoms present. At most 3.0×10^{15} fluorine atoms would be present if the SF_6 was completely stripped of its fluorine atoms. Assuming that all ions produced are collected, the number of ions produced per laser pulse is then calculated to be $\leq 6 \times 10^7$ per pulse for 1 torr SF_6 /1 torr CH_4 irradiated with 80 mJ at a 10 Hz frequency. Therefore, the ratio of the number of ions produced to the number of SF_6 molecules dissociated is about 10^{-7} per pulse. This agrees with Crim and co-workers who also found 10^{-7} fractional ionization ratios in their experiments.² Ion formation is therefore a minority process. This suggests that not all fluorine atoms are involved in ion production. Although the addition of as much as 5 torr of oxygen or argon to the above mixture does not appreciably change the amount of infrared laser energy absorbed by the system¹² the number of ions formed increases by a factor of 6 for oxygen and a factor of 4 for argon. It has been shown that buffer gases with vibrational frequencies close to $\nu_3(\text{SF}_6)$ will reduce the degree of SF_6 dissociation due to $V \rightarrow V$ exchange.¹³ The strong $V \rightarrow T$ relaxation due to added argon will also reduce the dissociation probability,¹⁵ although the increase in collisions leads to an abundance of vibrationally hot SF_6 . Under these conditions, the dominant pathway for atomic fluorine production is reaction (2). Similar behavior is observed for oxygen, but in addition to reducing the SF_6 multiphoton dissociation yield due to $V \rightarrow V$ exchange, it can participate in chemi-ionization reactions. Once atomic fluorine is produced in reaction (1) it can react with diatomic oxygen in a combustion reaction (6)¹⁰



or a combination reaction (7)



If reaction (6) takes place, the nascent oxygen produced can further react with CH_4 or $\text{CH}_3 \cdot$ to produce radicals which would lead to increased ion signals while simultaneously decreasing $\text{HF}^\#$ emission. On the other hand, if (7) is dominating under conditions where oxygen is present, both ion signal and HF fluorescence would be expected to decrease since a product molecule is formed, i.e., oxygen is acting as a fluorine scavenger. With 5 torr oxygen added to 1 torr each SF_6 and CH_4 , the fractional ionization rises by a factor of 6, which supports

the presence of reaction (6). HF^* is still observed under these reaction conditions and, therefore, it is probable that oxygen is acting as a collisional partner in a manner similar to that of argon rather than as a reactant. Since trace oxygen is a common contaminant in metal systems as well as bottled gases, one cannot preclude that some or possibly even all of the ionization seen with only SF_6 and hydrocarbons is not due to trace amounts of this gas. At the present time we have not resolved this question.

Reaction "quenchers" scavenge the free fluorine atoms before reaction with a hydrocarbon. Reactions of the types shown in Table II are predicted to be the most thermodynamically favored and are both feasible and probable under the reaction conditions reported here.¹⁰ If only free radical chemi-ionization occurs one would expect all of the ion signal to be quenched in situations where all of the free fluorine would be scavenged. This is not observed, as shown in Figure 3, where the effect of various scavengers on the ion signal of SF_6/CH_4 is shown. Even when 10 torr scavenger is added an ion signal can be detected. This suggests that yet another mechanism which leads to ion formation is occurring independent of atomic fluorine production. If the hydrocarbon has vibrational levels nearly resonant with the excited SF_6 molecule, then efficient $V \rightarrow V$ energy transfer can take place.

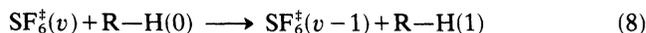


TABLE II
Enthalpy and free energy of formation of products of reaction
of scavengers with atomic fluorine^{a,b}

Reaction	(kcal/mol)	
	ΔH_f°	ΔG_f°
$2\text{F} + \text{CO} \rightarrow \text{F}_2\text{CO}$	-164.003	-145.757
$\text{F} + \text{NO} \rightarrow \text{NOF}$	-56.14	-47.497
$\text{F} + \text{NO}_2 \rightarrow \text{FNO}_2$	-52.77	-42.906
$\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$	-31.90	-31.833
$\text{F} + \text{N}_2\text{O} \rightarrow \text{FO} + \text{N}_2$	-164.003	-145.757

^a At 298 K.

^b Calculated from JANAF Thermochemical Tables, Second Edition, NBS Publications.

Successive collisions between the excited hydrocarbon and the excited SF₆ can lead to dissociation of the latter species and subsequent ion formation by reaction (4). For such a reaction to be significant its rate must be competitive with that of SF₆ dissociation.

Using deuterium as a probe of F atom production under the same experimental conditions as those involving hydrogen, we were able to monitor DF⁺ fluorescence from reaction (9)

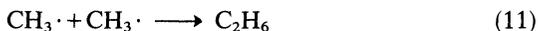


The DF fluorescence is sufficiently red-shifted from HF^{*} not to be passed by the HF filters in front of the IR detector.

Diatomic hydrogen behaves differently from all other scavengers, including deuterium. When 10 torr H₂ is added to the SF₆/CH₄ mixture, no ion signal is observed, presumably due to scavenging of all free fluorine atoms. The fluorescence lifetime of HF⁺ is observed to increase with increasing hydrogen partial pressure. At H₂ pressures where all ion signal was quenched the temporal behavior of HF fluorescence closely resembled that of a pure SF₆/H₂ mixture.⁴ Two mechanisms can be proposed to account for such behavior. (1) Thermal pyrolysis of the hydrocarbon to elemental carbon and hydrogen



and/or (2) radical recombinations producing stable saturated hydrocarbons such as ethane,



whose larger radicals do not possess the energetics necessary for ion formation.² The first mechanism is unlikely as the temperature in the reaction zone is not high enough for complete pyrolysis to occur. However, Woodin and Kajkowski¹⁴ have shown that SF₆ sensitized laser pyrolysis of methane under similar experimental conditions results in ethane production. Their data show methyl radical formation in the first step



followed by reaction (11). Therefore, the second mechanism postulated above is felt to be more likely in our experiments.

Experiments in which the hydrocarbon pressure was reduced below 1 torr are shown in Figures 4 and 5. At 1 torr SF₆ and 0.5 torr CH₄, the intensity of the ion signal is not stable with time but rather decays following first-order kinetics with a rate constant of $\sim 4 \times 10^3 \text{ s}^{-1}$. Adding 0.5 torr of hydrogen to this mixture results in a faster decay of the ion signal. The decay under such conditions is not unimolecular, as a plot of ln ion signal peak versus time is not linear. Such a falloff is more accurately described by a bimolecular rate expression.

$$\frac{d[\text{ion}]}{dt} = k[\text{ion}][\text{H}_2] \quad (13)$$

In contrast to the ion signal, the decrease in HF⁺ intensity of the same reaction mixtures (Figure 5) is linear over 10 minutes and also dependent on CO₂ laser pulses.

We had previously shown that at least 5.0×10^{14} F atoms are produced per laser pulse under our experimental conditions. At 0.5 torr CH₄ there are 1.5×10^{19} molecules present in the volume of our cell (900 cm³). From the ion signals for these experiments, we calculate that 2.5×10^{10} ions are formed per pulse initially. The fractional ionization is, therefore, two orders of magnitude greater than seen with equal pressures of SF₆ and CH₄. This implies that ion formation is a more efficient process under these conditions. However, the following conclusions are reached: (1) Not all fluorine atoms attack the hydrocarbon, (2) not all hydrocarbon radicals form ions, and (3) more than one hydrocarbon radical is needed for ion formation.

From these results, we are able to rank the various scavengers in order of their effectiveness of quenching reaction (3),



The above ordering is roughly in the order of decreasing rate constants for reaction with free fluorine.^{10,15,16}

This trend is the reverse order of the exothermicity and Gibb's free energy of the reaction of scavenger with atomic fluorine. Apparently, the best fluorine scavenging reactions, defined here as those which decrease ion production the most, have the largest positive heats of formation. Therefore, liberating a large amount of heat into the area of the reaction results in a relatively small decrease in ion signal compared with no scavenger at all. A higher temperature in the

reaction zone can enhance thermal ionization. The best fluorine scavenging reaction is also the least spontaneous. This reverse behavior is possibly due to the high electronegativity of the fluorine atom, which is highly reactive.

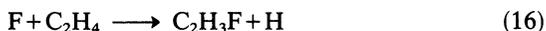
The reaction of ethane with atomic fluorine is expected to proceed via the same mechanism as that of methane



HF fluorescence from reaction (10) is observed to have comparable intensity and lifetime to that found in methane. The ion signal resulting from the reaction of ethane with fluorine is a factor of two smaller than that observed with methane. This may be because excited radicals (CH^* , CH_2^* , CH_3^*) are more difficult to produce from the larger ethyl radical.^{1,2} Also, ethane and atomic fluorine react in an eight-step sequence to yield ethylene as well as HF^\dagger .¹⁷



Other end products include C_4H_{10} , CH_3F , $\text{C}_2\text{H}_5\text{F}$ and $\text{C}_3\text{H}_7\text{F}$. These larger molecules also will not form small radicals, hence ions, easily. For this reason, production of ethylene from ethane is expected to result in low HF emission and little, if any, ion production. This is due to the fact that, unlike the alkanes, which undergo a hydrogen abstraction reaction to form radicals, ethylene will add fluorine across the double bond.¹⁷



Experiments of the type previously described in which ethylene was used as the hydrocarbon support this claim. The HF^\dagger fluorescence was a factor of three smaller than that of methane and no ion production was observed.

This last discussion will address the possible importance of negative charge carriers, which are also observed. It is probable that SF_6^- is the predominant negative species, formed by electron attachment to neutral SF_6 in a nondissociative process.



The metastable sulfur hexafluoride anion has a long lifetime with respect to autodetachment.¹⁸ However, if it is vibrationally hot from

absorption of infrared photons, it readily dissociates



Thus negative ions of SF_6^- and SF_5^- can be expected to be present. Subsequent chemistry of these species with small hydrocarbons such as CH_4 would be of considerable interest if it could lead to production of $\text{CH}_3\cdot$.

One possible reaction mechanism is



Reaction 19 is about 0.5 eV endothermic and should be possible if SF_6^- is sufficiently vibrationally hot. The analogous reaction of SF_5^- with CH_4 is not likely being several eV endothermic. Whether the $\text{CH}_3\cdot$ is formed by reaction (3) or reaction (19), the subsequent chemi-ionization reactions producing the positive ions discussed by Crim *et al.* are straightforward. From a direct mass spectrometric probe of the reaction zone, we hope to shed some light on the species produced in this reaction.

SUMMARY

We have shown that atomic fluorine produced by infrared multiphoton dissociation of SF_6 will yield fluorine atoms which can attack small hydrocarbons, abstracting a hydrogen to form small radicals and HF^+ . These small radicals can produce ions if electronically excited. At the present time we cannot present a mechanism for electronic excitation of these radicals, but can only say that it is a necessary step in the ion production sequence. The loss of energy by vibrationally hot HF through infrared fluorescence and the current resulting from collection of the ions on electrodes were monitored simultaneously. Both these signals have given valuable information as to the mechanism of ion production by laser irradiation of SF_6 /hydrocarbon mixtures.

Further experiments using unsaturated hydrocarbons and injection of the ions into a quadrupole mass spectrometer are currently in progress in an attempt to identify the ionic species. Other experiments to deduce the role of molecular and/or atomic oxygen in the ionization process are of interest.

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