SiF$_4$ IR Photodissociation: Gas phase reactions of SiF$_3$ with CH$_4$

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ABSTRACT

The infrared multiphoton dissociation (IRMPD) of SiF$_4$ in the presence of CH$_4$ has been studied using a tunable CO$_2$ TEA laser. The siliconated reaction products have been identified. A kinetic scheme has been proposed to explain the experimental results. The reaction rate constant of the trifluorosilyl radical, SiF$_3$, with CH$_4$ has been obtained from the numerical solution of the differential equation system associated to the kinetic mechanism proposed as well as from non-linear regression methods. It has been additionally found that this reaction occurs through two channels. The relative importance of each and their reaction rate constants have been determined as well.

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1. Introduction

In the last years, the interest in the study of the reactions involving silicon containing molecules has increased, essentially since they are used as precursors in processes such as chemical vapor deposition (CVD) of silicon films [1], laser synthesis of Si/C/N nanocomposites [2] or as impurity removal of silicon surfaces [3]. These molecules have been also used as "working molecules" in the laser isotope separation of silicon [4–9]. Silicon tetrafluoride, SiF$_4$, participates in these processes either as precursor or as product of the reactions initiated by other molecules.

SiF$_4$ in mixtures with H$_2$ and/or CH$_4$ is used in the chemical vapor deposition of SiC films [10–11]. A deep understanding of the processes involved in the SiC formation is of vital importance for obtaining films with adequate properties. SiF$_n$ and SiH$_n$F$_n$ radicals, which undergo gas phase reactions and play an important role in the film growing mechanism, are produced during the CVD process. However, there is scarce information available on the kinetics of these radicals. Thus, the study of the reactions of these radicals with gases used in the CVD of silicon containing films is relevant.

The infrared multiphoton dissociation (IRMPD) of molecules can be used to generate radicals for the study of gas phase reactions. The IRMPD of SiF$_4$ has been investigated by several authors under differ-

ent experimental conditions [12–15]. However, these experiments have not undertaken the study of the primary products of the dissociation nor of the reaction which take place following the laser pulse. In a previous work we have evidenced that, in the infrared multiphoton dissociation of SiF$_4$, SiF$_3$ and F radicals are generated through the rupture of the Si−F bond. The recombination reaction of these radicals to regenerate SiF$_4$ is the main reaction following the dissociation [16]. In that work, it has been proven, too, that the addition of H$_2$ as SiF$_3$ and F radicals' scavenger inhibits the recombination reaction. SiF$_3$H was the main product obtained in the SiF$_4$ IRMPD in excess of H$_2$.

In the present work the IRMPD of SiF$_4$ in mixtures with CH$_4$ has been investigated. The fraction of SiF$_4$ molecules dissociated, the amount of CH$_4$ consumed and the amounts of SiF$_3$H and SiF$_3$CH$_3$ products generated per pulse, as well as their CH$_4$ pressure dependence have been measured. A kinetic mechanism has been proposed to describe the results obtained. The reaction rate constant of the trifluorosilyl radical, SiF$_3$, with CH$_4$ has been obtained from the numerical solution of the differential equation system associated to the kinetic mechanism proposed as well as from non-linear regression methods. It has been additionally found that this reaction occurs through two channels. The relative importance of each and their reaction rate constants have been determined as well.

2. Experimental

The IRMPD of the SiF$_4$ (Matheson, 99.99%) in the presence of CH$_4$ (Alphagaz, 99%) was performed in a cylindrical Pyrex glass cell of 4 cm diameter and 10 cm length, with a cold finger and KCl windows

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sealed with araldite to both ends. A homemade multimode, pulsed, tunable TEA CO_2 laser with 1 J at 1 Hz output energy and 100 ns pulse length was used as IR radiation source for SiF_4 dissociation. The laser was tuned to the 9P(36), 1031.5 cm^{-1}, emission line which is resonant with the SiF_4 ν_3 vibrational mode (1031.8 cm^{-1}) [17], and was focused in the centre of the cell with a 12.7 cm focal length Ge lens.

The spatial profile of the multimode laser was taken to be homogeneous, *top hat*, so that the fluence in the cell was modeled by:

$$\Phi(r,z) = \begin{cases} \dfrac{\Phi_0}{1 + (Z/Z_R)^2} & r \le \omega(z) \\ 0 & r > \omega(z) \end{cases} \tag{1}$$

where Φ_0 is the laser fluence at the focus and Z_R the Rayleigh range. At the same time, in the propagation axis, the focusing was modeled by the following expression:

$$d(z) = d_0 \sqrt{1 + \left(\frac{z}{Z_R}\right)^2} \tag{2}$$

where z is the longitudinal coordinate and d_0 the beam diameter at the focus.

The beam diameter at the focus, 1 mm, was determined by measuring the diameter of the spot after the beam hits on a blackened glass.

The irradiated volume (V_i) was determined by integrating the beam area inside the Rayleigh range. The ratio of the cell volume, V_c, to the irradiated volume, V_i, was $V_c/V_i = 500$.

In all the experiments the SiF_4 partial pressure was 0.4 Torr (1 Torr = 133 Pa). The CH_4 pressure was varied in the range 0.04–5 Torr. The reactants and products were handled in a hydrocarbon free high-vacuum system.

The reactants and products partial pressures in the samples were determined by IR spectrometry with a FTIR spectrometer (Perkin Elmer, System 2000). In order to improve the signal-to-noise ratio, each spectrum was obtained from 40 scans registered with a resolution of 1 cm^{-1}. The dissociation progress was followed recording spectra every 1000 pulses in order to obtain significant variations in the reactants and products concentrations.

The reactants and products composition in each spectrum was determined using calibrated spectra of the different gases and a program based on non-linear regression techniques. Briefly, the program developed generates a synthetic spectrum in a selected wavenumber range from a linear superposition of the reference spectra of the different compounds (reactants and products). Each reference spectrum is assigned a weight factor. The synthetic spectrum is compared to the unknown spectrum to be analyzed through the mean square error (MSE) of the difference of both spectra with the weight factors as the fitting parameters. The Simplex of Nelder-Mead algorithm was implemented for the minimization of the MSE in a multidimensional space from which the partial pressures of the different compounds are obtained. The calculations were performed in the 800–1050 cm^{-1} wavenumber range for SiF_4, SiF_3H and SiF_3CH_3; and in the 2900–3150 cm^{-1} wavenumber range for CH_4. The reference spectra were obtained from calibration curves previously performed using pure samples of each compound. The absorbance detection limit was 0.008.

3. Results and discussion

Fig. 1 shows an IR spectrum of a typical sample of 0.4 Torr of SiF_4 and 1.6 Torr of CH_4 before and after irradiation with 5000 laser pulses. The SiF_4 main absorption band at 1031 cm^{-1}, as well as three peaks in the wavenumber range 975–1010 cm^{-1} corresponding to products formed are observed in the irradiated sample. These peaks can be assigned to the siliconated reaction products, SiF_3H
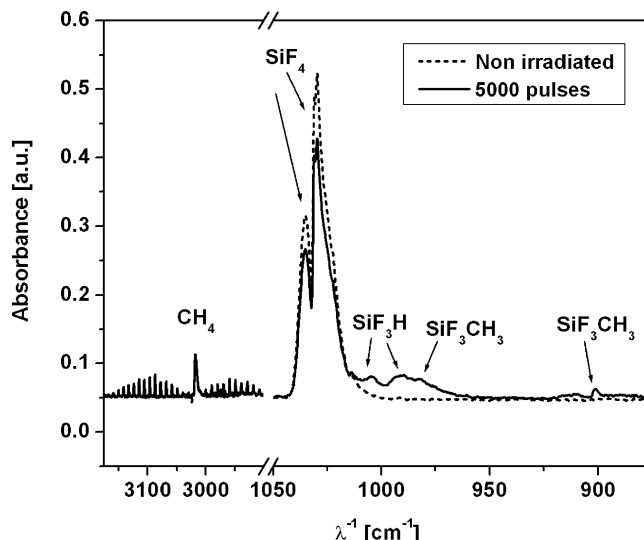

Fig. 1. Infrared spectra of a sample of 0.4 Torr of SiF_4 and 1.6 Torr of CH_4: before irradiation (dotted line) and after irradiation with 5000 laser pulses (solid line). The products SiF_3H and SiF_3CH_3 are observed.

and SiF_3CH_3, formed. The bands peaked at 990 and 1005 cm^{-1} would indicate the formation of SiF_3H [18,19] while those at 900 and 982 cm^{-1} would indicate the presence of SiF_3CH_3 [20,21].

The variation of the amount of reactants (SiF_4, CH_4) consumed in the cell with the number of laser pulses was determined in all the irradiated samples and a linear dependence was obtained as shown in Fig. 2 for a sample of 0.4 Torr of SiF_4 (solid line) and 0.5 Torr of CH_4 (dotted line). It was additionally observed that the amount of consumed CH_4 was approximately double than that of consumed SiF_4.

The variation with the number of laser pulses of the amounts of SiF_3H and SiF_3CH_3 produced in the cell was determined in all the irradiated samples and a linear dependence was obtained, too. This variation is exemplified in Fig. 3 for a sample of 0.4 Torr of SiF_4 and 0.5 Torr of CH_4.

The fraction of SiF_4 molecules dissociated per pulse, F, defined as:

$$F = 1 - \left(\frac{[SiF_4]_n}{[SiF_4]_0}\right)^{\frac{1}{n}} \tag{3}$$
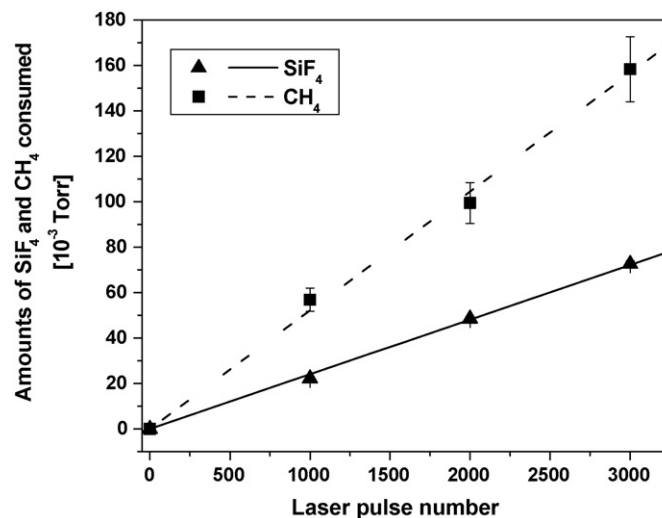

Fig. 2. Dependence of the amounts of SiF_4 and CH_4 consumed on the number of laser pulses for a sample of 0.4 Torr of SiF_4 and 0.5 Torr of CH_4.
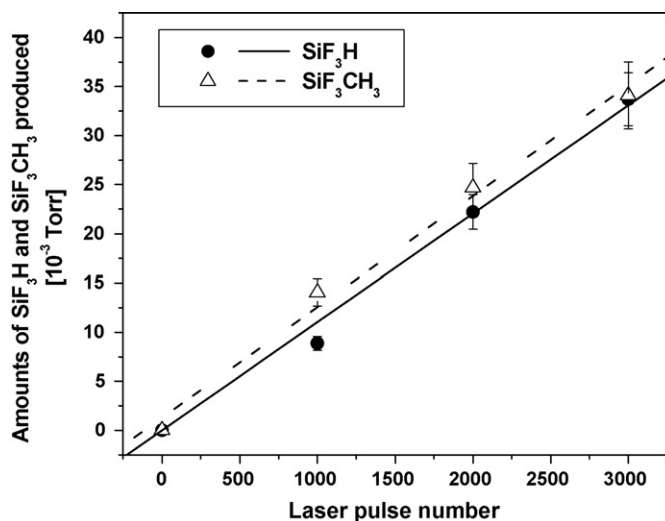
Fig. 3. Dependence of the amounts of SiF_3H and SiF_3CH_3 produced on the number of laser pulses for a sample of 0.4 Torr of SiF_4 and 0.5 Torr of CH_4.

where $[SiF_4]_0$ is the initial concentration of the reagent in the cell, $[SiF_4]_n$ is the concentration after the irradiation with n pulses, was determined for each sample.

As will be explained later on, the kinetics of the consumption of the generated radicals is sufficiently fast so that all reactions occur only in the irradiated volume. The time between laser pulses (1 s), at repetition rate of 1 Hz is sufficiently long so that diffusion processes take place and are complete. Therefore, a better estimator is the local SiF_4 dissociated fraction per pulse, that is, the SiF_4 fraction dissociated inside the irradiated volume which can be defined as:

$$\gamma = \frac{V_c}{V_i} F \qquad (4)$$

where V_c and V_i are the cell and irradiated volumes, respectively.

Fig. 4 shows the CH_4 pressure dependence of γ. In this figure, two well differentiated regimes dependent on CH_4 pressure, are observed. In the low pressure range, an increase of γ with an increase of acceptor gas pressure is observed. The dissociation increase with increasing CH_4 pressure would indicate the existence of a SiF_4 regeneration mechanism which would be important only
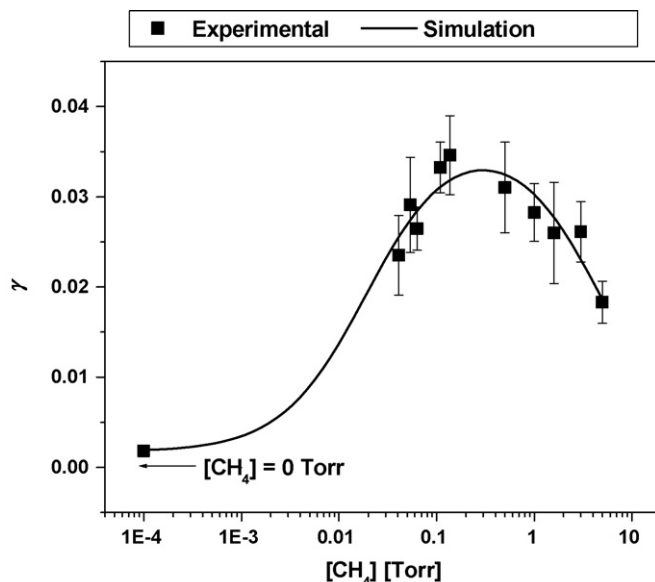

Fig. 4. Local fraction of SiF_4 dissociated per pulse, γ, vs. CH_4 partial pressure.

Table 1
Kinetic scheme used in the simulations.

Reaction		k	Ref.
(R.4)	$SiF_3 + F \rightarrow SiF_4$	$1.3\ 10^{-10}$ cm^3 molecule^{-1} s^{-1}	[16]
(R.5)	$SiF_3 + SiF_3 \rightarrow Si_2F_6$	$1.3\ 10^{-12}$ cm^3 molecule^{-1} s^{-1}	[16]
(R.6)	$F + F + M \rightarrow F_2 + M$	$6.0\ 10^{-34}$ cm^6 molecule^{-2} s^{-1}	[23]
(R.7a)	$SiF_3 + CH_4 \rightarrow SiF_3H + CH_3$	$2.8\ 10^{-11}$ cm^3 molecule^{-1} s^{-1}	This work
(R.7b)	$SiF_3 + CH_4 \rightarrow SiF_3CH_3 + H$	$2.8\ 10^{-11}$ cm^3 molecule^{-1} s^{-1}	This work
(R.8)	$F + CH_4 \rightarrow HF + CH_3$	$6.3\ 10^{-11}$ cm^3 molecule^{-1} s^{-1}	[22]

at very low acceptor gas pressure. In the high pressure regime, a decrease of γ with increasing CH_4 pressure is observed. This effect is caused by the deactivation of vibrationally excited SiF_4 in collisions with other sample components. An arrow superimposed in the figure indicates the value of γ in the absence of CH_4. The fact that in the absence of added acceptor gas the value of γ is not null indicates that the reactant regeneration is not complete.

The kinetic scheme listed in Table 1 was proposed to explain the experimental results obtained. The values of the reaction rate constants reported in this work have been obtained from the numerical solution of the differential equation system associated to this kinetic mechanism. However, as a first insight, the order of magnitude of these reaction rate constants can be estimated from simple arguments.

The laser excites a fraction of SiF_4 molecules, f_o, over the dissociation threshold. This fraction is reduced, in a pressure dependent amount, by collisions with different sample components, M.

$$SiF_4 + nh\nu \xrightarrow{f_0} SiF_4^* \qquad (R.1)$$

$$SiF_4^* + M \xrightarrow{k_2} SiF_4 + M \qquad (R.2)$$

$$SiF_4^* \xrightarrow{k_3} SiF_3 + F \qquad (R.3)$$

In consequence, the fraction f of SiF_4 molecules which effectively dissociates per pulse is given by:

$$f = \frac{1}{1 + \frac{[M]}{a}} f_0 \qquad (5)$$

where $a = k_3/k_2$ is the ratio of the bimolecular deactivation and the unimolecular dissociation rates. Therefore, in the irradiation volume and during the pulse length, (100 ns), the laser pulse dissociates a fraction f of SiF_4 molecules

$$\Delta[SiF_4]_{laser} = f[SiF_4]_0 \qquad (6)$$

and generates the same amounts of F and SiF_3 radicals

$$[F]_0 = [SiF_3]_0 = f[SiF_4]_0 \qquad (7)$$

Following the laser pulse and, depending on the acceptor gas pressure, reactions between radicals

$$SiF_3 + F \xrightarrow{k_4} SiF_4 \qquad (R.4)$$

$$SiF_3 + SiF_3 \xrightarrow{k_5} Si_2F_6 \qquad (R.5)$$

$$F + F + M \xrightarrow{k_6} F_2 + M \qquad (R.6)$$

or reactions between radicals and CH_4

$$SiF_3 + CH_4 \xrightarrow{k_7} Products \qquad (R.7)$$

$$F + CH_4 \xrightarrow{k_8} HF + CH_3 \qquad (R.8)$$

will take place.

The rate constants of reactions (R.4) and (R.5), k_4 (1.3 10^{-10} cm^3 molecule^{-1} s^{-1}) and k_5 (1.3 10^{-12} cm^3 molecule^{-1} s^{-1}), have been determined in a previous work [16]. The value of the rate constant of reaction (R.8), $k_8 = 6.4\ 10^{-11}$ cm^3 molecule^{-1} s^{-1}, has been reported in reference [22]. Data about the reaction (R.7) products or rate constant have not been reported to our knowledge. The value of the rate constant of reaction (R.6) in the low pressure regime reported by Ultee [23], $k_6 = 6\ 10^{-34}$ cm^6 molecule^{-2} s^{-1}, is much lower than that of reaction (R.5). Therefore, in the absence of CH$_4$, reaction (R.5) is the only reaction which competes with the recombination reaction with F radicals for the SiF$_3$ radical consumption and is responsible of the non-null value of γ.

Thus, the most relevant reactions are the F and SiF$_3$ recombination reaction (R.4) and the reactions of these radicals with CH$_4$, (R.7) and (R.8), so that the amount of SiF$_4$ regenerated per pulse is given by

$$\Delta[SiF_4]_{REG} = \frac{k_4 f[SiF_4]_0}{k_4 f[SiF_4]_0 + k_{max}[CH_4]} f[SiF_4]_0 \tag{8}$$

and, therefore, the net amount of SiF$_4$ molecules dissociated per pulse is

$$\Delta[SiF_4]_{NET} = \Delta[SiF_4]_{laser} - \Delta[SiF_4]_{REG}$$

$$= \frac{k_{max}[CH_4]}{k_4 f[SiF_4]_0 + k_{max}[CH_4]} f[SiF_4]_0 \tag{9}$$

In the high pressure regime, reactions (R.7) and (R.8) inhibit the F and SiF$_3$ radicals' recombination reaction (R.4). A critical methane pressure, $[CH_4]_c$, for which the F and SiF$_3$ radicals recombination reaction (R.4) and the reaction of CH$_4$ with one of these radicals (R.7) and (R.8) compete in equal terms can be obtained from Fig. 4. The reaction involved would be the faster between (R.7) and (R.8). Using Eq. (9), a maximum, k_{max}, between k_7 and k_8

$$k_{max}[CH_4]_c \approx k_4 f[SiF_4]_0 \tag{10}$$

is obtained. Estimations from Fig. 4 result in $f \approx 0.03$ and, the CH$_4$ pressure for which γ reaches half its maximum value, is approximately $[CH_4]_c \approx 0.02$ Torr. Since $[SiF_4]_0 = 0.4$ Torr the estimated rate constant is $k_{max} \approx 7\ 10^{-11}$ cm^3 molecule^{-1} s^{-1} which is of the same order of $k_8 = 6.4\ 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This rough estimation indicates that k_7 should be of the same order or less than k_8. Moreover, k_7 should be quite larger than 10^{-12} cm^3 molecule^{-1} s^{-1} since, if it were not so, Si$_2$F$_6$ would be formed via reaction (R.5) and this product has not been observed. On the other hand, it was found that the amount of methane dissociated doubles that of SiF$_4$ in agreement with the fact that both radicals must consume CH$_4$ in equal parts.

Although reaction (R.7) explains the increase of γ with the increase of CH$_4$ pressure, the proposed kinetic scheme does not explain the formation of the SiF$_3$H and SiF$_3$CH$_3$ products which have been clearly identified in the experiments.

In order to elucidate the formation mechanism of the silicon containing products, the dependence of the amount of CH$_4$ consumed per pulse, $\Delta[CH_4]$, on the amount of SiF$_4$ consumed per pulse, $\Delta[SiF_4]$, has been determined. A good linear correlation between them with a coefficient $R^2 = 0.97$ has been found as shown in Fig. 5 with $\Delta[CH_4]$ doubling $\Delta[SiF_4]$. For CH$_4$ pressures higher than 0.12 Torr, the dependence of the amounts of SiF$_3$H and SiF$_3$CH$_3$ produced per pulse, $\Delta[SiF_3H]$ and $\Delta[SiF_3CH_3]$, respectively, on $\Delta[SiF_4]$, has been determined as well. Fig. 6 shows that in this case linear relationships between these quantities with coefficients $R^2 = 0.98$ and $R^2 = 0.95$ for $\Delta[SiF_3H]$ and $\Delta[SiF_3CH_3]$, respectively, have been obtained, too. In addition, almost the same values of $\Delta[SiF_3H]$ and $\Delta[SiF_3CH_3]$ have been obtained, indicating that the amount of SiF$_4$ consumed per pulse is distributed fifty-fifty to generate SiF$_3$H and SiF$_3$CH$_3$.
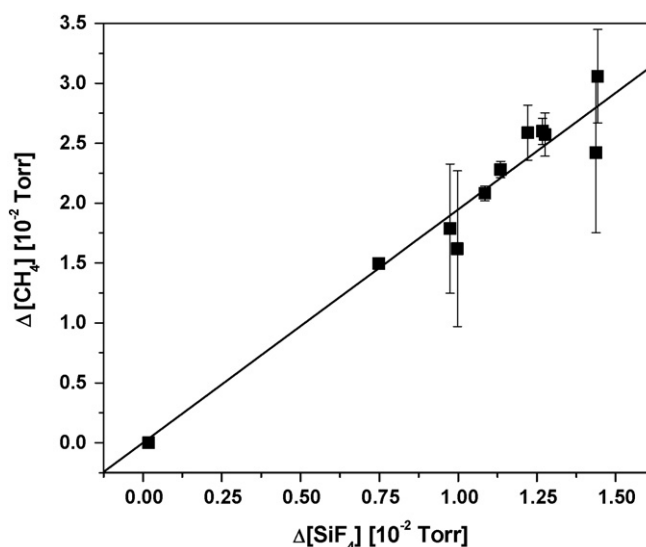

Fig. 5. Dependence of the amount of CH$_4$ consumed per pulse, $\Delta[CH_4]$, on the amount of SiF$_4$ consumed per pulse, $\Delta[SiF_4]$.

These experimental results suggest that the SiF$_3$ radical reacts with CH$_4$ through the following channels:

$$SiF_3 + CH_4 \xrightarrow{k_{7a}} SiF_3H + CH_3 \tag{R.7a}$$

$$SiF_3 + CH_4 \xrightarrow{k_{7b}} SiF_3CH_3 + H \tag{R.7b}$$

The CH$_3$ radicals generated in reactions (R.7a) and (R.7b) undergo self-reactions to generate C$_2$H$_6$. This product could only be evidenced in experiments performed with samples containing CH$_4$ partial pressures between 1 and 2 Torr irradiated with 5000 laser pulses. In these experiments about 80 mTorr of C$_2$H$_6$ were generated, the absorbance of which was about the detection limit of our spectrometer.

In the study of the IRMPD of SiF$_4$ in mixture with CH$_3$Cl as acceptor gas, reported in a previous work [16], the main products obtained were SiF$_3$H and SiF$_3$CH$_3$, while SiF$_3$Cl was only a minor product. The results of this experiment reinforce the experimental
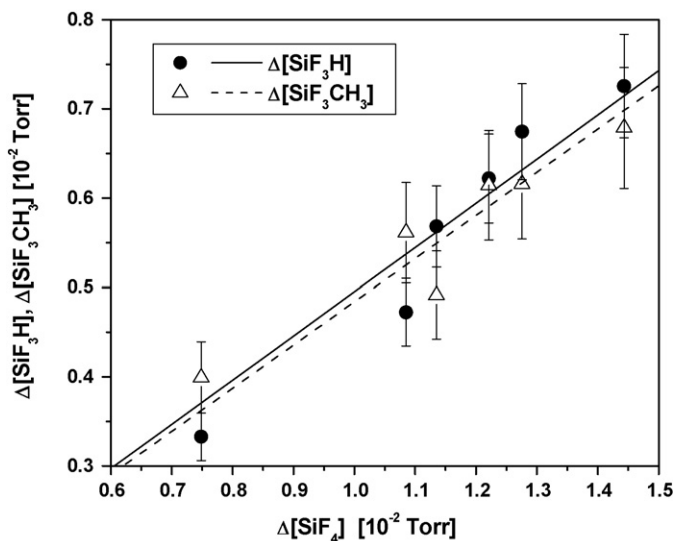

Fig. 6. Dependence of the amounts of SiF$_3$H and SiF$_3$CH$_3$ produced per pulse, $\Delta[SiF_3H]$ (solid line) and $\Delta[SiF_3CH_3]$ (dotted line), on the amount of SiF$_4$ consumed per pulse, $\Delta[SiF_4]$.

evidence shown in Figs. 5 and 6 and led us to propose the occurrence of reaction (R.7b) as a SiF_3 radicals sink.

Reactions (R.7a) and (R.7b) indicate that the ratio of the amounts of both products generated per pulse is the ratio of their reaction rate constants

$$\frac{\Delta [SiF_3H]}{\Delta [SiF_3CH_3]} = \frac{k_{7a}}{k_{7b}} \qquad (11)$$

As has been shown in Fig. 6, almost the same amounts of SiF_3H and SiF_3CH_3 are formed per pulse indicating that $k_{7a} \approx k_{7b}$.

In order to obtain the value of the reaction rate constant k_7, two programs have been developed. The first program performed the numerical integration of the differential equation system associated to the kinetic scheme of Table 1. The second program, adjusted the values of the reaction rate constants from the MSE minimization of the local SiF_4 dissociated fraction per pulse values predicted by the model to those of the experimental data. In the first program, the Runge-Kutta integration algorithm was used while in the second the Simplex of Nelder-Mead algorithm was again implemented.

Diffusion is neglected in the model since, as previously mentioned, inside the irradiated volume the radicals are consumed in much shorter times than the diffusion rates. The value of the reaction rate constant k_7 obtained from the model was 5.6 10^{-11} cm^3 molecule^{-1} s^{-1}.

The total sample pressure dependence of the fraction of SiF_4 molecules which effectively dissociate per pulse was used as an additional fitting parameter. The effective fraction of molecules dissociated by the laser was calculated from Eq. (3) and the ratio $a = k_3/k_2 = 5$ Torr was obtained from the simulation. This value indicates the pressure value at which the dissociation falls to half its value due to colisional quenching of the excited molecules by other sample components. In addition, the fraction of excited SiF_4 molecules with enough energy to undergo dissociation per pulse, f_0, was obtained and resulted in 3.7 %.

The solid line in Fig. 4 shows the result of the calculations with the model. An excellent correlation between experimental and calculated data is observed.

The values of the reaction rate constants k_{7a} and k_{7b} were obtained from the determined value of the global reaction rate constant of the SiF_3 radicals with CH_4, k_7, and resulted in $k_{7a} = k_{7b} = 2.8$ 10^{-11} cm^3 molecule^{-1} s^{-1}.

4. Conclusions

A TEA CO_2 laser has been used to study the IRMPD of SiF_4 in the presence of CH_4. The experiments have been performed in a static cell and the reactants and products concentration evolution have been analyzed by FTIR spectrometry. It has been found that the addition of CH_4 as acceptor gas inhibits the reactant regeneration reaction through SiF_3 and F radicals capture.

A kinetic scheme has been proposed to explain the experimental results. The set of coupled differential equations associated to this scheme has been solved and a very good agreement between experimental and calculated results has been obtained.

The rate constant of the SiF_3 radical reaction with CH_4, has been determined. The value obtained was $k_7 = 5.6$ 10^{-11} cm^3 molecule^{-1} s^{-1}. This value is approximately two and a half times the rate constant of the SiF_3 radical reaction with H_2 (2.2 10^{-11} cm^3 molecule^{-1} s^{-1}) [16]. This ratio of the reaction rate constants of the SiF_3 radicals with CH_4 and H_2, is in good agreement with the ratio of the reaction rate constants of the F radicals with CH_4 and H_2 [22].

Moreover, it has been determined that SiF_3H and SiF_3CH_3 are the only siliconated products formed in the reaction of the SiF_3 radicals with CH_4. It has been additionally found that, in the formation of these products, two channels with comparable reaction rate constants compete. The values of the reaction rate constants obtained were $k_{7a} = k_{7b} = 2.8$ 10^{-11} cm^3 molecule^{-1} s^{-1}.

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