Infrared multiphoton dissociation of SiF$_4$: gas phase reactions of SiF$_3$ with F and H$_2$

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Abstract

The infrared multiphoton dissociation (IRMPD) of pure SiF$_4$ and in mixtures with different gases was studied using a tunable CO$_2$ TEA laser. The initial dissociation step of the IRMPD of SiF$_4$ was found to be the decomposition into SiF$_3$ and F. The gas phase reactions of trifluorosilyl, SiF$_3$, with F and H$_2$ was investigated. A kinetic scheme was proposed to explain the experimental results. The set of coupled differential equations associated to this scheme was numerically solved. The rate constants of the SiF$_3$ + F $\rightarrow$ SiF$_4$ and SiF$_3$ + H$_2$ $\rightarrow$ SiF$_3$H + H reactions were determined.
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1. Introduction

Small gaseous silicon compounds are used as precursors in processes such as laser synthesis of silicon containing nanopowders and nanocomposites [1], chemical vapor deposition (CVD) of thin silicon films [2] and etching of silicon surfaces [3]. SiF$_4$ is the final product in fluorine systems of plasma etching and a silicon source for CVD. SiF$_n$ species of lower fluorination are also produced and their chemical reactions with other reactants control these processes. The thermochemical functions of SiF$_n$ and SiH$_n$F$_m$ compounds as well as of Si$_2$F$_6$ have been determined [4–6]. The gas phase SiF$_2$ reactions with several inorganic molecules and radicals have been extensively studied and rate constants are available [7,8]. There are several studies of reactions of SiF$_3$ radicals with organic compounds but only one rate constant reported of the reactions of these radicals with inorganic compounds [9].

In the last years, the infrared multiphoton dissociation (IRMPD) of natural abundance Si$_2$F$_6$ using a TEA CO$_2$ laser has been investigated to obtain a new method of sil-

icon isotope separation [10–15]. It was found that Si$_2$F$_6$ decomposed in highly isotopically selective manner to form SiF$_2$ and SiF$_4$ [12–16]. On the other hand, Lyman and Rockwood [17] have studied the IRMPD of SiF$_4$ in a H$_2$ bath to obtain silicon isotopic selectivity. Poor selectivity was found and the kinetics of the reaction was not studied.

In the present work, we have studied the IRMPD of SiF$_4$ alone and in mixtures with different acceptor gases. A kinetic mechanism was proposed to describe the results obtained in mixtures with H$_2$. Values for the SiF$_3$ radical reaction rate constants with F and H$_2$ as well as for self recombination were obtained from the solution of the associated coupled differential equations system.

2. Experimental

The IRMPD of SiF$_4$ was performed in a Pyrex glass cell of 4 cm in diameter and 10 cm in length, with KCl windows. The reactants and products were handled in a hydrocarbon free high-vacuum system. A homemade pulsed, tunable TEA CO$_2$ laser with 1 J at 1 Hz output energy and 180 ns pulse length was used as IR radiation source for dissociation. The laser was tuned to the 9P(36), 1031.5 cm^{-1}, emission line which is resonant with the SiF$_4$ v_3 vibrational mode (1031.8 cm^{-1}) [18,19], and was focused in the center of the cell with a 12.7 cm focal length Ge lens. The

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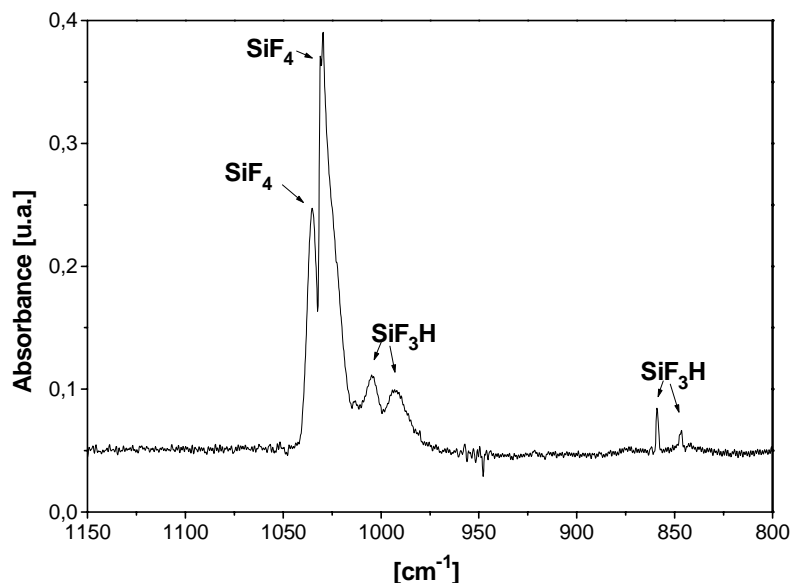(M.L. Azcárate).

Fig. 1. Infrared spectrum of 0.533 hPa of SiF_4 and 2.133 hPa of H_2 after irradiation with 5000 laser pulses.

diameter of the spot at the focus was 1 mm and the ratio of the cell volume, V_c, to the irradiated volume, V_i, was $V_c/V_i = 500$. In all the experiences the SiF_4 partial pressure was 0.533 hPa. The H_2 pressure was varied in the range 0.013–6.667 hPa in the experiments performed in a H_2 bath.

The sample partial pressure before and after each irradiation was determined by IR spectrometry with a Fourier transform IR (FT-IR) spectrometer, Perkin-Elmer, System 2000. IR spectra analysis was carried out at 1000 pulses irradiation steps due to the low SiF_4 dissociation rate. The reactant and product composition in each spectrum was determined using a program based on non-linear regression techniques. The calculations were performed in the 800–1100 cm^{-1} wavenumber range using calibrated spectra of the different gases. This analysis allowed SiF_3H and remnant SiF_4 concentrations in the cell to be determined with great accuracy.

Fig. 1 shows an IR spectrum of a typical sample of 0.533 hPa of SiF_4 and 2.133 hPa of H_2 after irradiation with 5000 laser pulses. The SiF_4 main absorption band at 1031 cm^{-1}, and the SiF_3H product bands [20,21] in the 850–1000 cm^{-1} wavenumber range are observed.

The gases used were SiF_4: Matheson, 99.99%; H_2: Union Carbide, 99.99%; O_2: Alphagaz, 99.9995%, CH_3Cl: Union Carbide, 99.5%; N_2: Praxair, 99.998%; CH_4: Alphagaz, 99%.

3. Results and discussion

The net local SiF_4 dissociated fraction is defined as

$$\gamma = \frac{V_c}{V_i} \left(1 - \left(\frac{[SiF_4]_n}{[SiF_4]_0} \right)^{1/n} \right) \tag{1}$$

where n is the number of laser pulses, $[SiF_4]_0$ the initial concentration of the reagent in the cell and $[SiF_4]_n$ is the concentration after the irradiation with n pulses. This magnitude is defined locally in the irradiated volume and is linked to the global dissociation per pulse in the cell volume through the V_i/V_c volume ratio.

The values of γ obtained in the IRMPD of pure SiF_4 and in mixtures with different acceptor gases are presented in Table 1.

In the thermal decomposition of SiF_4 breaking a single Si–F bond is the preferred path with a bond dissociation enthalpy of 167.47 kcal/mol [4]. The initial dissociation step for the IRMPD of SiF_4 was also found to be the decomposition into SiF_3 and F (2c), since $SiHF_3$ was the main siliconated product in presence of excess H_2 and CH_4.

A large increase in the fraction of molecules dissociated per pulse was obtained in the presence of CH_4, H_2 or CH_3Cl. This effect could be explained in terms of two different mechanisms: (a) the overcoming of the rotational bottleneck [22] to dissociation, typical of the IRMPD of small molecules, or (b) the inhibition of a possible SiF_4 regeneration reaction. The rotational bottleneck to dissociation is

Table 1
Apparent dissociated fraction of 0.533 hPa of SiF_4 in the presence of 2.133 hPa of different gases

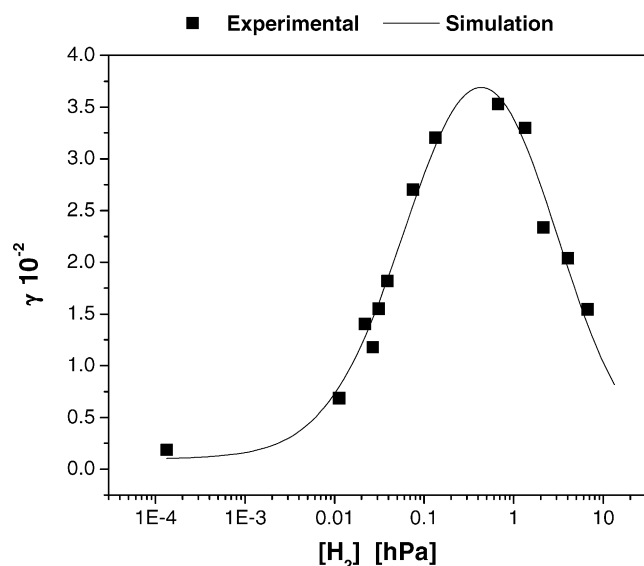| Sample composition	$\gamma \times 10^{-2}$
SiF_4	0.19
$SiF_4 + CH_4$	2.24
$SiF_4 + H_2$	2.34
$SiF_4 + CH_3Cl$	1.22
$SiF_4 + N_2$	<0.05
$SiF_4 + O_2$	<0.05

Fig. 2. Net local SiF_4 dissociated fraction (γ) vs. H_2 pressure.

overcome with the addition low pressures of a buffer gas. However, the effect of the addition of O_2 and N_2 was a decrease in the fraction of SiF_4 dissociated per pulse to values below the detection limit as a consequence of the collisional deactivation of the excited molecules [22,23]. The enhancement in the IRMPD of SiF_4 in the presence of acceptor gases would be therefore related to the inhibition of the SiF_4 regeneration reaction through some mechanism dependent on the reactivity of the scavenger gas and not to a physical process.

H_2 and CH_4 are the most efficient scavenger gases as can be inferred from the dissociation fractions listed in Table 1. The photodissociation of SiF_4 using H_2 as scavenger gas was studied in order to confirm the process of reagent regeneration.

The values of γ for different H_2 pressures are shown in Fig. 2. Two well-differentiated regimes dependent on the H_2 pressure are observed. In the high-pressure regime, the decrease of γ with increasing H_2 pressure is caused by the collisional physical quenching of the IRMPD, as with the addition of O_2 and N_2. This effect can be explained through the following mechanism:

$$SiF_4 + nh\nu \overset{f}{\rightarrow} SiF_4^* \tag{2a}$$

$$SiF_4^* + M \overset{k_0}{\rightarrow} SiF_4 + M \tag{2b}$$

$$SiF_4^* \overset{k_1}{\rightarrow} SiF_3 + F \tag{2c}$$

where the fraction f of highly excited molecules which, in a low collisional regime, would be dissociated is reduced in a quantity that depends on the total pressure, M, in the following way:

$$f_1 = \frac{k_1}{k_1 + k_0[M]} f \tag{3}$$

In the low pressure regime, the steady increase of γ with increasing H_2 pressure suggests the occurrence of a mechanism of reagent regeneration which is inhibited by the addition of H_2. This mechanism can be described as

$$SiF_3 + F \overset{k_2}{\rightarrow} SiF_4 \tag{4a}$$

$$SiF_3 + H_2 \overset{k_3}{\rightarrow} SiF_3H + H \tag{4b}$$

$$F + H_2 \overset{k_4}{\rightarrow} HF + H \tag{4c}$$

A first estimation of the recombination reaction rate constant k_2 can be obtained from the critical H_2 concentration, $[H_2]_C$, defined as the H_2 concentration for which γ reaches half its maximum value. Under these conditions the recombination reaction competes with the reaction (4c) for F consumption as follows:

$$k_2[SiF_3]_0 \approx k_4[H_2]_C \tag{5}$$

The estimated value of k_2 was calculated from Eq. (6) with $[H_2]_C \approx 0.067\,hPa$, $[SiF_4]_0 = 0.533\,hPa$ (the initial pressure of reagent used in all the experiences), $k_4 = 2.5 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ reported in [24], and the f value obtained from the maximum value of γ in Fig. 2 and resulted in

$$k_2 \approx k_4 \frac{[H_2]_C}{f[SiF_4]_0} \approx 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1} \tag{6}$$

This value evidences a very efficient recombination; if radicals are not scavenged, the regeneration of SiF_4 is a one collision process.

As shown in Fig. 2, the value of γ for very low pressures of H_2, and in particular in the absence of H_2, is not zero indicating that not all the SiF_3 and F radicals recombine to regenerate the reagent. This could be due to wall reaction losses. However, for the pressure range of this work, the diffusion times are of the order of dozens of milliseconds, while the characteristic radical recombination time is of the order of some microseconds. This would suggest the existence of an alternative channel of radical consumption which competes with the recombination reaction. Two possible radical sinks would be

$$SiF_3 + SiF_3 \overset{k_5}{\rightarrow} Si_2F_6 \tag{7a}$$

$$F + F + M \overset{k_6}{\rightarrow} F_2 + M \tag{7b}$$

The rate of the thermolecular reaction (7b), $k_6 = 6 \times 10^{-34}\,cm^6\,molecule^{-2}\,s^{-1}$, reported by Ultee [25] has not been considered in our estimates since in the pressure range of this work its rate was much lower than the estimated value of k_2. Therefore, in the absence of H_2 reaction (7a) is the only reaction that competes with SiF_3 and F radical recombination. Thus, the rate of reaction (7a) can be estimated from the calculated value of k_2 and the fraction
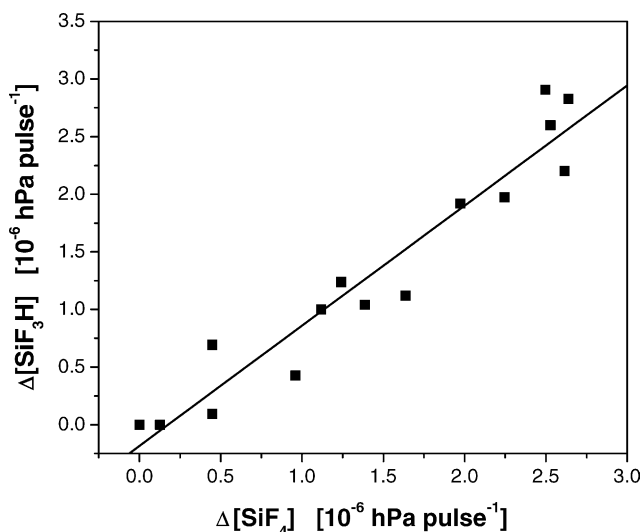
Fig. 3. Concentration of SiF$_3$H product formed per pulse vs. net amount of dissociated reagent per pulse.

of SiF$_4$ dissociated per pulse in absence of H$_2$. The amount of net reagent dissociated per pulse is

$$\Delta[SiF_4]_{NET} \approx f[SiF_4]_0 - \frac{k_2}{2k_5 + k_2} f[SiF_4]_0 \qquad (8)$$

where the first term accounts for the amount of photolyzed reagent and the second for the fraction regenerated via reaction (4a). In excess of H$_2$ we can suppose that all SiF$_3$ radicals produced react with H$_2$ through (4b), and thus, γ_{max} represents the real fraction of SiF$_4$ dissociated by the laser while in the absence of H$_2$, this fraction is reduced by the occurrence of (4a), so the net fraction of SiF$_4$ dissociated per pulse can be approximated by γ_{min}. From these considerations and Eq. (8) the relative importance between radical consumption channels (4a) and (7a) is

$$\frac{\Delta[SiF_4]_{NET}}{f[SiF_4]_0} \approx \frac{2k_5}{2k_5 + k_2} \approx \frac{\gamma_{min}}{\gamma_{max}} \qquad (9)$$

Fig. 2 shows that in the absence of H$_2$ the SiF$_4$ dissociation is 25 times smaller than its maximum value, thus the estimated value results in $k_5 \approx 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

The product SiF$_3$H is clearly identified in Fig. 1 confirming the occurrence of reaction (4b). However, the rate constant of this reaction has not been reported to our knowledge.

Fig. 3 shows the amount of SiF$_3$H product formed per pulse versus the net amount of reagent dissociated per pulse. A good linear correlation is found within the experimental error with a $R^2 = 0.94$ coefficient. The quantum yield of SiF$_3$H, Φ_{SiF_3H}, is unity at high H$_2$ pressure as expected from the proposed kinetic scheme. However, at low H$_2$ pressure the Φ_{SiF_3H} should be lower than 1 since another siliconated compound is being formed. The fact that Φ_{SiF_3H} remains ≈ 1 in the complete pressure range indicates that

$$k_3[H_2] \gg k_5 f[SiF_4]_0 \qquad (10)$$

This constraint together with the assumption that the rate of reaction of SiF$_3$ with H$_2$ should be comparable to the rate of reaction of SiF$_3$ with F, results in k_3 values in the range 10^{-12} to 10^{-11} cm^3 molecule^{-1} s^{-1}.

In order to improve our estimates and obtain more accurate values of the reaction rate constants, a non-linear least-squares regression program using these rates as adjustable parameters was performed to fit the experimental γ and [SiF$_3$H] data. Table 2 lists the complete kinetic scheme used for the calculations.

The program solves numerically the set of coupled differential equations associated to the kinetic scheme using the estimated values of the reaction rate constants as seed. The calculated and measured values of γ and [SiF$_3$H] per pulse for each H$_2$ pressure are compared and the reaction rate constants are modified so as to minimize the mean quadratic error. Diffusion is neglected in the model since inside the irradiated volume the radicals are consumed in much shorter times.

Fig. 2 shows the dependence of γ on H$_2$ pressure. The solid line is 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 obtained from the model, are in very good agreement with the estimated values as shown in Table 2. Different seeds were used in the simulation and in every run the same values of the parameters were obtained evidencing that the set of parameters obtained did not correspond to a local minimum of the mean quadratic error. On the other hand, it is important to stress that the good correspondence between the calculated and the estimated values of the rate constants indicates that the result of the simulations is not an artifact.

The pressure dependence of the IRMPD was used as an additional fitting parameter. The fraction of molecules dissociated by the laser was calculated from Eq. (3) and the ratio $k_1/k_0 = 2.67$ hPa was obtained from the simulation indicating the pressure value at which the dissociation falls to its half value due to the quenching. The real fraction of molecules dissociated per pulse was 5% and was obtained from the high H$_2$ pressure data extrapolating Eq. (3) to zero pressure. Therefore, the amount of radicals generated per pulse in the irradiated volume was

$$[SiF_3]_0 = [F]_0 = \frac{1.7 \times 10^{15}}{2.67 + P_{total}} \text{ molecules cm}^{-3} \text{ per pulse}$$
$$(11)$$

where P_{total} is in hPa.

Reaction (7a) was proposed as a sink of SiF$_3$ radicals since in the absence of H$_2$ the regeneration of SiF$_4$ is not complete. Fig. 4 shows a simulation result of the amount of reagent dissociated and the amounts of products generated versus H$_2$ pressure. This simulation was performed for a sample in the range of pressures used in this work irradiated with 5000 pulses. In Fig. 4 the concentration of Si$_2$F$_6$

Table 2
Kinetic scheme used in the simulations

Reaction no.	Reaction	k	Reference
(1)	$SiF_4 + nh\nu \rightarrow SiF_3 + F$	See text	This work
(2)	$SiF_3 + F \rightarrow SiF_4$	1.3×10^{-10} cm^3 molecule^{-1} s^1	This work
(3)	$SiF_3 + H_2 \rightarrow SiF_3H + H$	2.2×10^{-11} cm^3 molecule^{-1} s^{-1}	This work
(4)	$F + H_2 \rightarrow HF + H$	2.45×10^{-11} cm^3 molecule^{-1} s^{-1}	[14]
(5)	$SiF_3 + SiF_3 \rightarrow Si_2F_6$	1.3×10^{-12} cm^3 molecule^{-1} s^{-1}	This work
(6)	$F + F + M \rightarrow F_2 + M$	6.0×10^{-34} cm^6 molecule^{-2} s^{-1}	[15]

was increased in a factor of 20 for a better visualization. The maximum amount of Si_2F_6 predicted in the absence of H_2 after 5000 pulses is 2.67×10^{-3} hPa. Even though the Si_2F_6 absorbance coefficient at 992 cm^{-1} is quite large, (≈ 0.1 hPa^{-1} cm^{-1}) [14], the low concentration predicted results in an absorbance value below the limit of detection of the FT-IR spectrometer.

It should be mentioned that the reaction (7a) is quite exothermic ($\Delta H = 94.76$ kcal mol^{-1}) [4] and allows an alternative channel (12b)

$$SiF_3 + SiF_3 \xrightarrow{k_a} Si_2F_6 \qquad (12a)$$

$$SiF_3 + SiF_3 \xrightarrow{k_b} SiF_4 + SiF_2 \qquad (12b)$$

The channel (12b), originated from the unimolecular decomposition of the highly excited Si_2F_6, both regenerates the SiF_4 and is an alternative sink of SiF_3 radicals with a final siliconated product different from Si_2F_6. If we assume that the reaction (12b) were the only channel of SiF_4 regeneration, the ratio of the real to the net fraction of molecules dissociated per pulse (Eq. (9)) in absence of H_2 would not exceed the value of 2 while the experimentally obtained value is 25. Therefore, the recombination reaction (4a) must exist and it must be important. Then, considering the occurrence of reaction (4a) and both channels of reaction (7a) in ab-

sence of H_2 Eq. (9) becomes

$$\frac{\Delta[SiF_4]_{net}}{f[SiF_4]_0} \approx \frac{2k_{5a} + k_{5b}}{2k_{5a} + 2k_{5b} + k_2} \approx \frac{\gamma_{min}}{\gamma_{max}} \qquad (13)$$

In this case, channel (12a) is clearly a sink of radicals. Channel (12b), on the other hand, is a source of product as well as a sink of radicals. Assuming that the reaction (7a) occurs either through channel (12a) or through channel (12b), the estimated value for the rate constant of the reaction (7a), $k_5 = k_{5a} + k_{5b}$, represents 2 or 4% of the value of the rate constant of reaction (4a), respectively. Therefore, independently of the relative weight of each channel, the global reaction rate constant k_5 is always much smaller that the recombination reaction rate constant k_2.

4. Conclusions

A TEA CO$_2$ laser was used to study the IRMPD of pure SiF$_4$ and in mixtures with different acceptor gases. The experiments were performed in a static cell and the reactants and products concentrations were analyzed by FT-IR spectrometry. As in the thermal decomposition, the main dissociation channel in the IRMPD was the rupture of a Si–F bond.

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

The recombination of SiF$_3$ and F radicals turned out to be the main reaction channel in the pure sample resulting in an effective SiF$_4$ dissociated fraction per pulse 25 times lower than that produced by the laser. The rate constants of the SiF$_3$ radical reactions with F and H$_2$ ((4a) and (4b)), as well as an effective value for the rate constant of the SiF$_3$ radicals sink reaction (7a) were obtained using the reported value in the literature of the rate constant of reaction (4c). The values obtained were $k_2 = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, $k_3 = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k_5 = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.
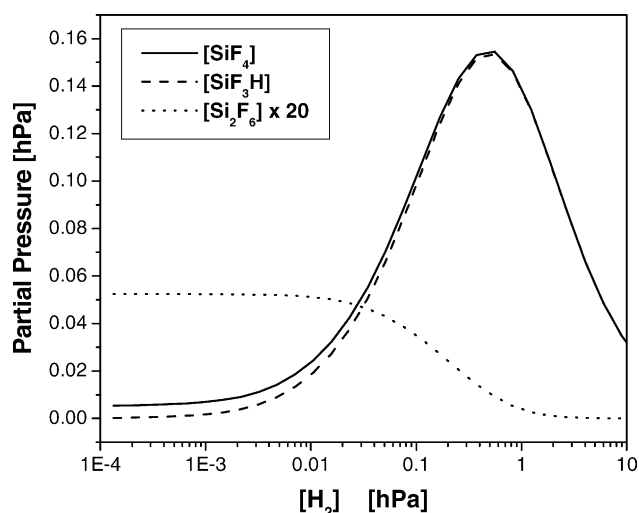
Fig. 4. Simulated concentrations of dissociated reagent and products formed vs. H$_2$ pressure.

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