Optimization of the infrared multiple-photon dissociation of SiF$_4$ to increase the isotopic selectivity

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Abstract. The influence of laser fluence and wavelength as well as of the sample pressure on the infrared multiple-photon dissociation (IRMPD) of SiF$_4$ and H$_2$ mixtures has been studied. Different lines of the 9.4 $\mu$m emission band of a TEA CO$_2$ laser have been used as excitation sources. A power law dependence of the fraction of molecules dissociated per pulse on the laser fluence was found. The optimization of the IRMPD of silicon tetrafluoride was performed by varying both SiF$_4$ and H$_2$ pressures. The IRMPD spectrum exhibits a red shift of ~ 12 cm$^{-1}$ produced by the anharmonicity of the molecular vibrations. Moreover, the isotopic selectivity of the IRMPD of SiF$_4$ has been determined with wavelengts shifted to the red and the blue of the 9P(36) line which is quasi-resonant with the $\nu_3$ mode of $^{28}$SiF$_4$. The maximum values were obtained with the 9P(32) emission line which has the least overlap with the absorption bands of the less abundant species.

1. Introduction

The potential commercial applications of the different silicon isotopes has encouraged the development of different laser isotope separation techniques for this compound. An increase in the thermal conductivity of silicon wafers enriched in $^{28}$Si with respect to that of natural abundance silicon wafers has been recently found [1-4]. This has promoted the search of new applications of isotopically pure materials in the semiconductor industry. The heat removal of electronic devices, which is a limiting factor of the power and commutation speed that can be achieved, would be greatly enhanced by the use of $^{28}$Si in their manufacture.

Infrared Multiple-Photon Dissociation (IRMPD) is a laser isotope separation technique which could be successfully applied to molecules containing silicon isotopes. This would require the choice of an adequate "working molecule". IRMPD with TEA CO$_2$ lasers has been used for the determination of isotopic selectivity of silicon containing compounds using different working molecules [5–10, 12].

The most promising results have been achieved with Si$_2$F$_6$. In these works the dependence of the enrichment coefficient in $^{28,30}$Si on different parameters such as the laser wavelength and fluence and the reactant pressure has been studied [12-15]. The dissociation mechanism and the product formation has been determined as well. The main advantages of this compound are that is dissociated with a high
yield at low fluences and only one product is obtained. The main drawbacks are its high production cost and that since this molecule has two silicon atoms, it may contain different isotopic mixtures such as $^{28}\text{SiF}_3 - ^{29,30}\text{SiF}_4$, which diminishes the IRMPD efficiency for $^{29}\text{Si}$ and $^{30}\text{Si}$. On the other hand, $\text{Si}_2\text{F}_6$ is quite unstable and, therefore, difficult to use in an industrial scale [16]. Arai et al. [14], have developed a flux system for the production of silicon isotopic enrichment at a larger scale and have produced some grams of $^{28}\text{Si}$ (98 – 99%), $^{29}\text{Si}$ (12%) and $^{30}\text{Si}$(20-30%). Okada and Takeuchi [17] have found enrichment factors larger than 5 for $^{29}\text{Si}$ and 10 for $^{30}\text{Si}$ in $\text{Si}_2\text{F}_6$ cooled in an adiabatic expansion of a molecular jet surpassing the values obtained at room temperature. In 2004, Yokoyama et al. [18] studied the IRMPD of $\text{Si}_2\text{F}_6$ with two CO$_2$ laser wavelengths and found a significant increase in the dissociation efficiency and enrichment factors of 200 and 50 for $^{29}\text{Si}$ and $^{30}\text{Si}$ respectively, at a total pressure of 2 Torr. IRMPD of $\text{Si}_2\text{F}_6$ [19, 20] with an free electron laser produced enrichment factors much lower than those obtained with CO$_2$ laser.

The molecules containing only one silicon atom that have been investigated so far [5–11] are not produced in a large scale and this could limit their use as working molecules in large scale silicon isotope separation. Although silicon tetrafluoride (SiF$_4$) is largely used in the semiconductor industry, it has been scarcely studied as a possible working molecule in the Si enrichment process by IRMPD. SiF$_4$ composition is determined by the natural abundance of the three silicon isotopes: $^{28}\text{Si}$ (92.23%), $^{29}\text{Si}$ (4.67%) and $^{30}\text{Si}$ (3.10%). The vibrational frequencies of the $\nu_3$ mode of the different isotopomers $^{28}\text{SiF}_4$, $^{29}\text{SiF}_4$ and $^{30}\text{SiF}_4$, 1031.8, 1022.9 and 1014.4 cm$^{-1}$ [21], respectively, are quasi-resonant with the emission lines of the 9.4 $\mu$m band of the CO$_2$ laser. SiF$_4$ IRMPD has been studied under different experimental conditions [22-25]. However, these investigations have not dealt with the study of the effect of the laser fluence and wavelength variation in the IRMPD, which is relevant for the optimization of the dissociation process and, consequently, for the isotopic enrichment. The dependence of the SiF$_4$ IRMPD with a CO$_2$ laser has been studied at Los Alamos Scientific Laboratory [20] and an enrichment coefficient of 1.11 in both $^{29,30}\text{Si}$ was obtained.

In a previous study we have determined that in the SiF$_4$ IRMPD the radicals SiF$_3$ and F are generated, which, in turn, react with each other to regenerate silicon tetrafluoride [26]. We have also proved that the addition of scavenger gases such as H$_2$, CH$_4$, CH$_3$Cl inhibits the occurrence of the radical recombination reaction by capturing the radicals SiF$_3$ and F. The optimization of the IRMPD of SiF$_4$ requires in first place, the adequate choice of the acceptor gas for the radicals generated in the dissociation. In previous studies [26, 27] we have demonstrated that similar maximum values of the fraction of molecules dissociated per pulse, $\gamma$, were obtained in mixtures with H$_2$ and CH$_4$. IRMPD of SiF$_4$ with H$_2$ [26] as scavenger gas has the advantage of generating only one silicon containing product, SiF$_3$H, which facilitates monitoring the dependence of the dissociation evolution on the laser pulse number. The following kinetic scheme describes the reactions that take place in the presence of H$_2$:

$$\text{SiF}_4 + n\nu \rightarrow \text{SiF}_3 + \text{F} \quad (1)$$

$$\text{SiF}_3 + \text{F} \rightarrow \text{SiF}_4 \quad (2)$$

$$\text{SiF}_3 + \text{H}_2 \rightarrow \text{SiF}_3\text{H} + \text{H} \quad (3)$$

$$\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H} \quad (4)$$

In this work we have studied the influence of the laser fluence (energy by unit area) and wavelength as well as of the sample pressure in the IRMPD of SiF$_4$ in mixtures with H$_2$. We have also undertaken the study of the isotopic selectivity in the IRMPD of SiF$_4$ with different emission lines of the P branch of 9.6 $\mu$m band of a TEA CO$_2$ laser.
2. Experimental

The IRMPD of the SiF$_4$ (Matheson, 99.99%) in the presence of H$_2$ (Union Carbide 99.99%) varying the pressure and the laser fluence was performed in a cylindrical Pyrex glass cell of 4 cm diameter and 10 cm length, with a cold finger and KCl windows sealed with araldite to both ends. A homemade multimode, pulsed, tunable TEA CO$_2$ laser with an output average energy of 1 J at 1 Hz 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$_4$ $\nu_3$ vibrational mode (1031.8 cm$^{-1}$) [28]. The laser radiation was focused into the centre of the cell with a 12.7 cm focal length Ge lens and a beam diameter of 1 mm was obtained at the focus. The laser energy was varied combining F$_2$Ca flats of different thickness so that the fluence in the centre of the cell varied in the 40 - 120 J cm$^{-2}$ range. The ratio of the cell volume, V$_c$, to the irradiated volume, V$_i$, was V$_c$/V$_i$ = 500. The study of the SiF$_4$ IRMPD dependence on laser fluence was carried out in mixtures of 0.4 Torr of SiF$_4$ and 1.6 Torr of H$_2$.

The reactants and products partial pressures in the samples were determined by IR spectrometry with a FTIR spectrometer (Perkin Elmer, System 2000). The dissociation progress was followed recording spectra every 500 pulses in order to obtain significant variations in the reactants and products concentrations. 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 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. The SiF$_4$ concentration was determined by analyzing the 900 - 1050 cm$^{-1}$ wavelength range, where the maximum absorbance band centered at 1031 cm$^{-1}$ occurs. Two wavelength ranges were analyzed for the product SiF$_3$H: the first one, 900 - 1050 cm$^{-1}$, where the peaks at 995 and 1005 cm$^{-1}$ corresponding to the $\nu_4$ mode are found, and the other, 800 - 900 cm$^{-1}$, where the peaks at 859 and 845 cm$^{-1}$ corresponding to the $\nu_2$ and $\nu_5$ modes [29, 30], respectively, are found. This analysis allowed the reactant, SiF$_4$, and product, SiF$_3$H, amounts to be determined with good precision. The reference spectra were obtained from calibration curves previously performed using pure samples of each compound. The absorbance detection limit was 0.008.

The fraction of SiF$_4$ molecules dissociated per pulse, F, defined as

$$F = 1 - \left( \frac{[\text{SiF}_4]_n}{[\text{SiF}_4]_0} \right)^{1/n}$$

(5)

where [SiF$_4$]$_0$ is the initial concentration of the reagent in the cell and [SiF$_4$]$_n$ is the concentration after irradiation with $n$ pulses, was determined for each sample. The kinetics of the generated radicals consumption is sufficiently fast so that all reactions occur only in the irradiated volume [26]. Diffusion processes take place at longer time intervals and are completed between laser pulses (1 s). Therefore, a more useful estimator is the local SiF$_4$ fraction of molecules dissociated per pulse, that is, the SiF$_4$ fraction of molecules dissociated inside the irradiated volume which can be defined as:

$$\gamma = \frac{V_c}{V_i} F$$

(6)

The study of the SiF$_4$ IRMPD dependence on laser wavelength was carried out in mixtures of 0.4 Torr of SiF$_4$ and 0.5 Torr of H$_2$. The laser was tuned to different emission lines of the of the 9.4 $\mu$m P branch. In order to obtain enough energy for SiF$_4$ dissociation a 60 % reflectivity Ge output coupler was used for the emission lines from 9P(36) to 9P(44) while an 85 % reflectivity ZnSe output coupler was used for the emission lines from 9P(46) to 9P(52). The curvature radius of both output couplers was 10 m.

The laser wavelength influence on the isotopic selectivity of the SiF$_4$ IRMPD was studied in a cylindrical Pyrex glass cell of 3.6 cm diameter and 15 cm length, with a cold finger and KCl windows.
sealed with araldite to both ends. The laser radiation was focused into the centre of the cell with a 10 cm focal length Ge lens. The laser average output energy was 1.6 J and the irradiation wavelengths used were: 1035.46 cm\(^{-1}\) 9P(32), 1033.48 cm\(^{-1}\) 9P(34), 1031.46 cm\(^{-1}\) 9P(36), 1029.43 cm\(^{-1}\) 9P(38) and 1025.28 cm\(^{-1}\) 9P(42).

The reactant, SiF\(_4\), and product, SiF\(_3\)H, isotopic composition were determined with a quadrupolar mass spectrometer, Extranuclear, EMBA II. The isotopic composition of SiF\(_4\) in non-irradiated and in irradiated samples was determined from the analysis of the intensities of the peaks with \(m/e = 85, 86\) and 87 \((I_{85}, I_{86}, I_{87})\) corresponding to the ions \(^{28}\)SiF\(_3^+\), \(^{29}\)SiF\(_3^+\) and \(^{30}\)SiF\(_3^+\), respectively [31]. The isotopic composition of SiF\(_3\)H was determined from the analysis of the intensities of the peaks with \(m/e = 67, 68\) and 69 corresponding to the \(^{28}\)SiF\(_2^+\)H+, \(^{29}\)SiF\(_2^+\)H+ and \(^{30}\)SiF\(_2^+\)H+ ions, respectively [32]. The mass spectrum of SiF\(_4\) also presents peaks at \(m/e = 66, 67\) and 68 \((I_{66}, I_{67}, I_{68})\), corresponding to the \(^{28}\)SiF\(_2^+\)H, \(^{29}\)SiF\(_2^+\)H and \(^{30}\)SiF\(_2^+\)H ions, but their intensities are less than 0.5 % of the intensity of the peak corresponding to the \(^{29}\)SiF\(_3^+\) ion [31]. Therefore, the contribution of SiF\(_4\) to the intensities of these peaks was disregarded.

3. Results and discussion

3.1. Laser fluence effect in the IRMPD of SiF\(_4\)

Figure 1 shows the dependence of the local SiF\(_4\) fraction of molecules dissociated per pulse, \(\gamma\), on the laser fluence at the beam waist, \(\Phi\). A typical potential law dependence on laser fluence, \(\gamma \sim \Phi^\beta\) [33], has been found with \(\beta = 2.39\).

![Figure 1](image-url)

**Figure 1**: Local SiF\(_4\) fraction of molecules dissociated per pulse, \(\gamma\), vs. laser fluence at the beam waist, \(\Phi\).

3.2 Pressure effect on SiF\(_4\) IRMPD

Both the reactant and scavenger gas pressure effect on the IRMPD of SiF\(_4\) has been studied.

Figure 2 shows the H\(_2\) pressure dependence of the IRMPD for samples containing 0.4, 1 and 3 Torr of SiF\(_4\). In the low pressure regime, an increase of the local SiF\(_4\) fraction of molecules dissociated per pulse with increasing scavenger gas pressure up to a H\(_2\) pressure of 0.5 Torr is observed in mixtures with 0.4 Torr of SiF\(_4\). This effect is a consequence of the inhibition of the reagent regeneration by the addition of H\(_2\).

A decrease of \(\gamma\) with increasing scavenger gas pressure is observed in all the gas mixtures for H\(_2\) pressures larger than 0.5 Torr. This effect is caused by the vibrational deactivation of excited SiF\(_4\) molecules by V-T energy transfer in collisions with the scavenger gas molecules [34, 35].
collisional deactivation mechanism does no depend on the reactant concentration within the experimental error.

Figure 3 shows the SiF₄ pressure dependence of the IRMPD for samples containing 1, 3, 10 and 20 Torr of H₂. As it can be seen, the local SiF₄ fraction of molecules dissociated per pulse does not depend on SiF₄ pressure. In mixtures with equal SiF₄ and H₂ concentrations, the recombination reaction between radicals generated in the IRMPD of SiF₄ is not completely inhibited.

Figure 2. Local SiF₄ fraction of molecules dissociated per pulse dependence on H₂ pressure for different SiF₄ pressures

Figure 3. Local SiF₄ fraction of molecules dissociated per pulse dependence on SiF₄ pressure for different H₂ pressures

3.3 Wavelength effect on SiF₄ IRMPD

Figure 4 shows IR multiple-photon dissociation spectrum of a mixture of 0.4 Torr of SiF₄ and 0.5 Torr of H₂ in the 1031.46 - 1014.47 cm⁻¹ wavelength range, 9P(36) – 9P(52), respectively. The linear absorption spectrum is included for comparison. An increase of the local SiF₄ fraction of molecules dissociated per pulse as the laser emission wavelength is shifted to the red of the linear absorption maximum of the ²⁸SiF₄ isotopomer, 1031.8 cm⁻¹. This behaviour caused by the anharmonicity of the first vibrational levels is typical of small molecules [34]. It has been also observed in the IRMPD of other silicon containing molecules such as SiF₃Cl [5].

Figure 4. Wavelength dependence of the local SiF₄ fraction of molecules dissociated per pulse superimposed on the linear absorption spectrum
The IRMPD spectrum presents a redshift of \(~ 12 \text{ cm}^{-1}\) with respect to the linear absorption spectrum. This result is consistent with the results of the study of the IRMPD of SiF\(_4\) performed by Akulin et al. [25] with two wavelengths. In this study one wavelength was kept fixed at 1029.4 cm\(^{-1}\), 9P(38), while the other was varied including emission lines of the P branch of the 9.4 \(\mu\)m band as well as of the R branch of the 10.6 \(\mu\)m band. These authors observed a 20 fold increase in the dissociation of SiF\(_4\) as the second wavelength was shifted to the red of the fixed wavelength.

3.4 Isotopic selectivity

The analysis of the IR spectra registered for each experiment every 500 pulses allowed to determine the evolution of the amounts of reactant dissociated and of product generated per pulse in the reaction cell. Since the contribution of the minor isotopic species \(^{29}\text{SiF}_4\) and \(^{30}\text{SiF}_4\) to the spectrum in the 1000 – 1040 cm\(^{-1}\) range is small (5 % and 3 %, respectively) and the absorption bands of these species, overlap with that of the most abundant species, \(^{28}\text{SiF}_4\), centred at 1031 cm\(^{-1}\) [21, 28], the partial pressures of these isotopomers could not be quantified. Thus, the SiF\(_4\) remnant fraction determined by IR spectrometry was the remnant amount of the major isotopomer \(^{28}\text{SiF}_4\).

Figure 5 shows the mass spectra of a non-irradiated mixture of 0.45 Torr of SiF\(_4\) and 1 Torr of H\(_2\) and of a mixture irradiated with 3000 pulses of the 9P(34) line, 1033.48 cm\(^{-1}\). As a result of the SiF\(_4\) reactant dissociation, a decrease of the intensities of the masses 85, 86 and 87 is observed. In addition, an increase of the intensities of the masses 67, 68 and 69 is observed as a consequence of the SiF\(_3\)H product formation.

![Mass spectra of a non-irradiated mixture of 0.45 Torr of SiF\(_4\) and 1 Torr of H\(_2\) and of another irradiated with the 9P(34) line, 1033.48 cm\(^{-1}\).](image)

Figure 5. Mass spectra of a non-irradiated mixture of 0.45 Torr of SiF\(_4\) and 1 Torr of H\(_2\) and of another irradiated with the 9P(34) line, 1033.48 cm\(^{-1}\).

The fraction of molecules of each SiF\(_4\) isotopic species, \(F_i\) \((s = 28, 29, 30)\), dissociated per pulse in the reaction cell (equation 5) can, in principle, depend on the irradiation wavelength [29, 30]. The remnant amount of each isotopic species \(s\) of the reactant, \([^{\text{i}}\text{SiF}_4]_0\), after \(n\) pulses is given by the following expression:

\[
[^{\text{i}}\text{SiF}_4]_n = (1 - F_i)^n [^{\text{i}}\text{SiF}_4]_0
\]

(7)

where \([^{\text{i}}\text{SiF}_4]_0\) is the amount of that species before irradiation. At the same time, after \(n\) pulses, the amount of an isotopic species \(s\) of the product, \([^{\text{SiF}_3\text{H}}]_n\), in the reaction cell can be expressed as:
\[ [^{19}\text{SiF}_3\text{H}]_n = (1 - (1 - F_p)^n)[^{19}\text{SiF}_3]_0 \]  \hfill (8)

The isotopic enrichment factor both in the reactant $^{29,30}\alpha$ as in the product $^{29,30}\beta$, is defined as:

\[
^{29,30}\alpha = \frac{F_{28}}{F_{29,30}}
\]  \hfill (9)

Considering that the intensity of each peak in the mass spectrum is proportional to the partial pressure of its associated compound, the ratios of the different species peaks enables to determine the isotopic selectivity both in the reactant and in the product. The $\alpha$ and $\beta$ factors are obtained from the expressions (7) and (8) with the definitions of $X$ and $Y$ given in equations (12) and (13)

\[
^{29,30}\alpha = \frac{F_{28}}{1 - (1 - F_{28}) \left( \frac{X_n}{X_0} \right)^\frac{1}{n}}
\]  \hfill (10)

\[
^{29,30}\beta = \frac{Y_n}{X_0}
\]  \hfill (11)

\[
^{29,30}X = \frac{[^{28}\text{SiF}_3]}{[^{29,30}\text{SiF}_4]} = \frac{I_{85}}{I_{86,87}}
\]  \hfill (12)

\[
^{29,30}Y = \frac{[^{28}\text{SiF}_3\text{H}]}{[^{29,30}\text{SiF}_3\text{H}]} = \frac{I_{67}}{I_{68,69}}
\]  \hfill (13)

where subscripts 0 and $n$ indicate the non-irradiated sample and the sample irradiated with $n$ pulses, respectively. Thus, the enrichment factors are determined from the peak intensities ratios of the mass spectra and the parameter $F_{28}$ obtained from IR spectrometry.

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**Figure 6.** Wavelength dependence of the isotopic enrichment factor $\alpha$ in the reactant

**Figure 7.** Wavelength dependence of the isotopic enrichment factor $\beta$ in the product
Figures 6 and 7 show the enrichment factors $\alpha$ and $\beta$, respectively, obtained with the different laser emission lines. In both figures the linear IR absorption spectrum was superimposed for comparison.

Equation (9) indicates that the enrichment factors determined in the reactant and in the product should be identical. As it can be seen in figures 6 and 7, both enrichment factors have a similar behaviour: both factor decrease with decreasing wavelength and the factor corresponding to the isotopomer 30 is larger than that of the 29. These results evidence that as the wavelength decreases, the overlap between the laser emission line and the minor species absorption bands increases. In consequence, $F_{29,30}$ increases, this effect being more noticeable for the heaviest isotope.

4. Conclusions

SiF$_4$ IRMPD was investigated with a pulsed TEA CO$_2$ laser. The local SiF$_4$ fraction of molecules dissociated per pulse was found to have a potential law dependence on laser fluence.

In the study of the dependence of the SiF$_4$ IRMPD on the partial pressures of the reactants, the largest local SiF$_4$ fraction of molecules dissociated per pulse has been obtained for SiF$_4$ pressures between 0.16 and 0.8 Torr and for H$_2$ pressure of 1 Torr. SiF$_4$ IRMPD must be carried out in excess of H$_2$ since for equal SiF$_4$ and H$_2$ concentrations the radical recombination reaction is not completely inhibited.

The SiF$_4$ IRMPD spectrum determined in the P(36) – P(52) wavelength range of the P branch of the 9.4 $\mu$m band of the $^{12}$CO$_2$ laser presents a redshift of ~ 12 cm$^{-1}$ with respect to the IR linear absorption spectrum due to the anharmonicity of the molecular vibrations. In order to complete the spectrum, the wavelength range could be expanded by using a $^{13}$CO$_2$ laser.

The enrichment factors in the SiF$_4$ reactant and in the SiF$_3$H product, $^{29,30}\alpha$ and $^{29,30}\beta$, respectively, have been determined with different emission lines of the P branch of the 9.4 $\mu$m band of a TEA CO$_2$ laser. Both factors decrease with decreasing wavelength as a consequence of the increase of the overlap between the laser emission lines and the absorption bands of the minor isotopic species. The maximum values have been obtained with the 9P(32) emission line which presents the least overlap with the absorption bands of the minor isotopomers.

The optimization of SiF$_4$ IRMPD varying both the reactant, SiF$_4$, and the scavenger gas, H$_2$, pressures enabled to obtain a maximum value of 2.8 for $^{29}\alpha$ which is 2.5 times larger than the only value reported in the literature [33].

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