Infrared Multiphoton Si Isotope Selective Dissociation of Phenyltrifluorosilane under Free Electron Laser Irradiation

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Received: January 27, 2003; In Final Form: August 6, 2003

We have used free electron laser (FEL) at the IR FEL Research Center, Research Institute for Science and Technology, Tokyo University of Science, Japan. The multiphoton absorption of infrared radiation induced dissociation of phenyltrifluorosilane ($PhSiF_3$) in a batch reactor. End product analysis from IR MPD of neat $PhSiF_3$ and the mixture of $PhSiF_3$ and Br_2 shows that the main dissociation channels are (1) the elimination of SiF_3 and (2) the elimination of H. Silicon isotopes have been enriched under the FEL irradiation of neat $PhSiF_3$ at 961 cm^{-1} (abundance of ^{30}Si in $PhSiF_3$ was increased from 3.10 ± 0.03% to 12.3 ± 0.1%) and 925 cm^{-1} (abundance of ^{28}Si in $PhSiF_3$ was increased from 92.2 ± 0.9% to 96.5 ± 0.9%).

Introduction

Stable silicon isotopes become useful materials in the electronic industry. Highly enriched silicon isotopes are used to provide a material with enhanced optical, electronic, and/or heat dissipation characteristics.[1] For instance, ^{30}Si is used for NTD (neutron transmutation doping) to produce homogeneous *n*-type silicon semiconductors. Recently, the idea of a silicon-based nuclear spin quantum computer[2] caused additional interest to pure silicon isotopes.

These requests demand an effective isotope separation process for Si. Laser isotope separation (LIS) using infrared multiphoton dissociation (IR MPD) is one of the most promising ways to satisfy the demand because of its high selectivity. Traditionally, LIS is studied with TEA-CO_2 lasers. However, the tunability of a TEA-CO_2 laser is too narrow to select the most appropriate working material. A free-electron laser (FEL) is continuously tunable over a broad frequency range. On the other hand, the temporal, frequency, and spatial profiles of a FEL beam are different from ones for a TEA-CO_2 laser. Recently, it was demonstrated that multiphoton dissociation with an infrared FEL can be isotopically selective, resulting in significant enrichment of carbon,[3−9] nitrogen,[10] and silicon[11] isotopes.

Silicon has three stable isotopes:[12] ^{28}Si (92.23%), ^{29}Si (4.67%), and ^{30}Si (3.10%). Silicon isotopes have been enriched by IR MPD reactions induced with infrared lasers.[11,13−18] Except for the earliest demonstration,[13] which was infrared dissociation of SiF_4 (with low enrichment factor and high decomposition fluence), all of the recent work has been with the species Si_2F_6. Although Si_2F_6 has certain advantages for LIS of silicon (high isotopic selectivity and efficiency of IR MPD), it has a few disadvantages as well. The industrial application of Si_2F_6 is complicated by the fact that Si_2F_6 is rather unstable.[11] Another limitation is that the presence of two silicon atoms in Si_2F_6 decreases the efficiency of LIS for ^{29}Si and ^{30}Si, because these minor isotopes are presented in the molecule mainly in combination with ^{28}Si. Thus, it remains reasonable to continue the search for other chemical compounds for the effective enrichment of silicon isotopes.

One may consider that organosilanes are promising compounds for the LIS of silicon, because IR MPD of organosilanes $RSiH_3$ (R = ethyl, *n*-butyl, phenyl) has been observed[19−21] at relatively low fluence and the appearance of SiH_4 was detected. It is also expected that fluorine-substituted organosilane $PhSiF_3$ has good efficiency of IR MPD that leads to the formation of the isotopically enriched SiF_4. In contrast to Si_2F_6, the molecule $PhSiF_3$ is stable, and it has just one silicon atom. Phenyltrifluorosilane possesses strong infrared absorption at 860 and 970 cm^{-1}. The infrared spectrum of this molecule in the 970 cm^{-1} spectral region is shifted for different silicon isotopes by a larger value than the spectrum of Si_2F_6. Therefore, $PhSiF_3$ may be a suitable candidate for the LIS of silicon. In this work, the first study of Si isotope selective IR MPD of phenyltrifluorosilane under FEL irradiation is presented.

Experimental Section

The experiments have been performed at the IR FEL Research Center, Research Institute for Science and Technology, Tokyo University of Science, Japan.[22] This laser produces pulsed IR radiation that is continuously tunable over the 5−16 μm range with a bandwidth of 0.7%. FEL runs at a 5 Hz repetition rate. The light output consists of macropulses of about 2 μs duration. The macropulse energy was varied from 8 to 17 mJ. Each macropulse consists of a train of micropulses that are 350 ps apart. The micropulse duration is 2 ps.

Dissociation was carried out in a focused beam of the FEL. The diameter of the laser beam was first reduced from 5 to 0.6 cm by a spherical mirror with the focal length of 1300 cm, and then the laser beam was focused into the center of a cylindrical stainless steel cell of 12 cm length and 4 cm diameter by a Zn−Se lens with the focal length of 25 cm. The cell was fitted with a pair of Zn−Se windows. The laser beam intensity

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10.1021/jp034214p CCC: $25.00

measured near the focal point had a Gaussian spacial distribution. The waist of the beam had a radius of 0.42 mm. The single macropulse energy density in the waist center (fluence) was varied in different experiments from 1.4 to 3.1 J/cm^2 through the change of the FEL macropulse energy. The effective irradiated volume, $V_f = 36$ mm^3, is only a minor fraction of the total volume of the cell, $V_{gas} = 1.5 \times 10^5$ mm^3. The laser-beam divergence measured was no larger than the diffraction limit.

The experiments were performed at room-temperature, irradiating samples of neat $PhSiF_3$ with a natural abundance of Si isotopes and in some cases of $PhSiF_3$ and Br_2. The initial pressure of $PhSiF_3$ was varied from 0.05 to 2 Torr. The pressure of Br_2 was 5 Torr. On-line analysis of the working mixture was carried out by FTIR and quadrupole mass spectrometers. The isotopic enrichment was represented by the $PhSiF_3^+$ signals from the mass spectrometer. The amount of $PhSiF_3$ and products during irradiation was evaluated from the corresponding IR absorption peaks and the mass spectrum.

Process Kinetics

Dissociation in a focused laser beam is conveniently characterized by the yields Y_i ($i = 28$ for ^{28}Si, etc.). These yields are equal to the number of Ph^iSiF_3 molecules, dissociated per pulse divided by the total number of such molecules in the effective local volume V_f. In the case of Gaussian beam propagation the following expression[23] is used:

$$V_f = \frac{2\sqrt{\pi}(\pi\omega^2)^2}{3\lambda} \tag{1}$$

where ω is the laser beam radius at the focal point and λ is the wavelength of laser radiation. Y_i is calculated from the fractions of dissociated phenyltrifluorosilane measured, C_i, and the known irradiation time t:

$$Y_i = -\frac{V_{gas}}{V_f}\frac{\ln(1 - C_i)}{Ft} \tag{2}$$

where V_{gas} is the total volume of the working mixture, F is the repetition frequency of the laser macropulses. The ratio Y_i/Y_k is the isotopic selectivity S_{ik} of dissociation.

The fluence Φ was calculated from the laser macropulse energy E by the following expression:

$$\Phi = \frac{E}{\pi\alpha^2} \tag{3}$$

Unimolecular dissociation probabilities P_i at the center of the focal region may be smaller or greater than Y_i, depending on the character of the function $P_i(\Phi)$. In the usual approximation, i.e., $P_i(\Phi) \sim \Phi^\gamma$, dissociation probability and yield are proportional to each other, i.e., $P_i = gY_i$, if the yield, Y_i, is small. The proportionality coefficient g is equal to 0.85 at $\gamma = 2$, 2.55 at $\gamma = 3$, and 4.53 at $\gamma = 4$.[24]

Results and Discussion

To estimate the isotopic shifts in $PhSiF_3$, we carried out ab initio calculations of the IR absorption spectrum of this molecule (Figure 1a) and compared it with the experimental one (Figure 1b). The calculations were performed with the DFT Becke3LYP[25] method as implemented in GAMESS[26] and Dunning's D95-(d,p)[27] basis set was used. The calculated frequencies were not scaled. One can see from Figure 1a,b that the agreement between the calculations and the experiment is very good in the range from 500 to 1500 cm^{-1}. The disagreement in line positions is less than 1%. Using this ab initio method, we calculated infrared absorption bands of $PhSiF_3$ with different silicon isotopes (Table 1). It follows from Table 1 that the biggest isotope shift corresponds to the 970 cm^{-1} spectral region (Si−F stretching mode): ~8 cm^{-1} between ^{28}Si−F and ^{29}Si−F, and ~8 cm^{-1} between ^{29}Si−F and ^{30}Si−F. Therefore, this spectral region was chosen for Si isotope selective multiphoton dissociation of the target molecule.

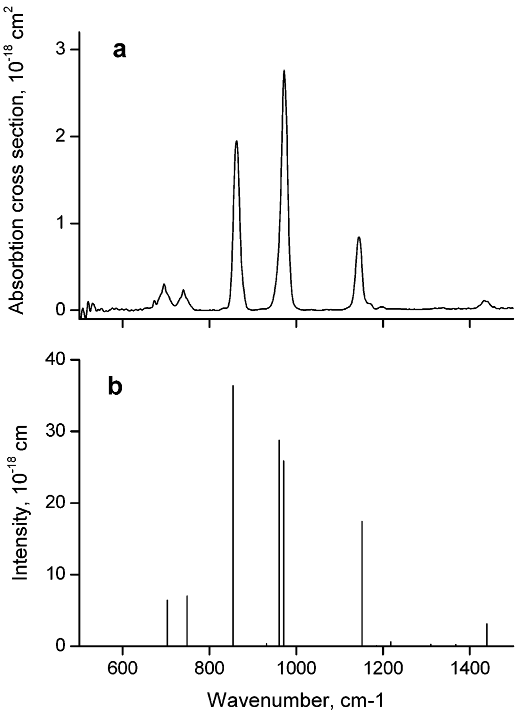

Figure 1. (a) Gas-phase IR absorption spectrum of $PhSiF_3$ (cross section). (b) Calculated IR absorption spectrum of $PhSiF_3$.

TABLE 1: Measured and Calculated IR Spectrum (cm^{-1}) of $PhSiF_3$

$PhSiF_3$ (exp)	$Ph^{28}SiF_3$ (calc)	$Ph^{29}SiF_3$ (calc)	$Ph^{30}SiF_3$ (calc)
696	702.9	702.9	702.9
740	748.5	748.5	748.5
861	854.6	849.7	845.1
971	960.5	952.1	944.4
977	971.1	962.5	954.4
1145	1151.6	1150.4	1149.3
1435	1439.3	1439.3	1439.3

The example of the measured dynamics of the IR spectrum of the reaction mixture during multiphoton dissociation of $PhSiF_3$ under the action of the FEL at 961 cm^{-1} is presented in Figure 2. One can see the absorption peaks of $PhSiF_3$ at 861, 971, 977, and 1145 cm^{-1} are decreasing, and a new absorption peak at 1031 cm^{-1} is appearing and increasing. We assigned this new peak to SiF_4 because of its location and shape (the spectrum of neat SiF_4 is shown in Figure 3). Additionally, the appearance of C_6H_6 and SiF_3H were detected from the analysis of IR absorption and mass spectra of the working mixture. After the volatile gas products were collected at 77 K, a residual pressure was observed that could be attributed only to the formation of H_2.

The infrared spectrum before and after irradiation provided quantitative measures of the amount of SiF_4 versus the amount of $PhSiF_3$ in each experiment. The example of the dependence is shown in Figure 4. The slope of the linear fit to those points

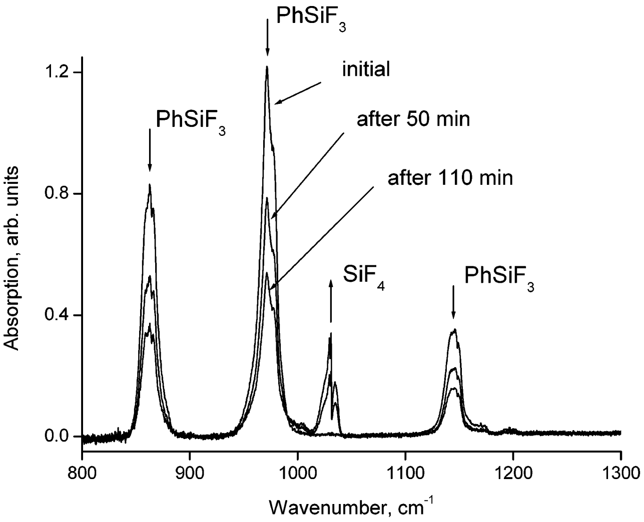

Figure 2. Change of the IR spectrum of the reaction mixture during IR MPD of neat $PhSiF_3$ at wavenumber 961 cm^{-1} and fluence 3.1 J/cm^2.

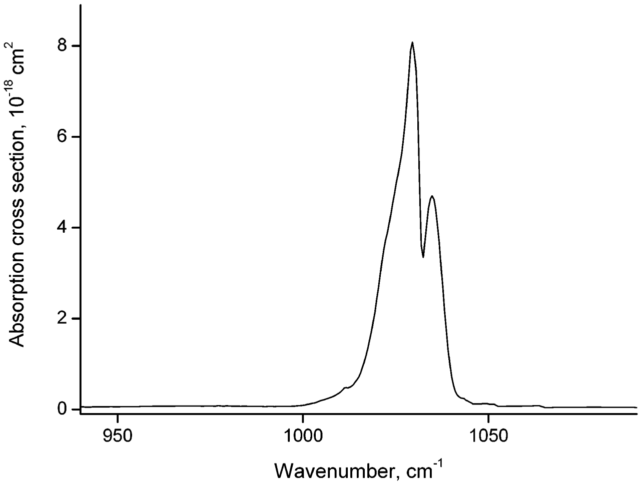

Figure 3. Measured IR absorption spectrum of neat SiF_4 (pressure = 0.16 Torr).

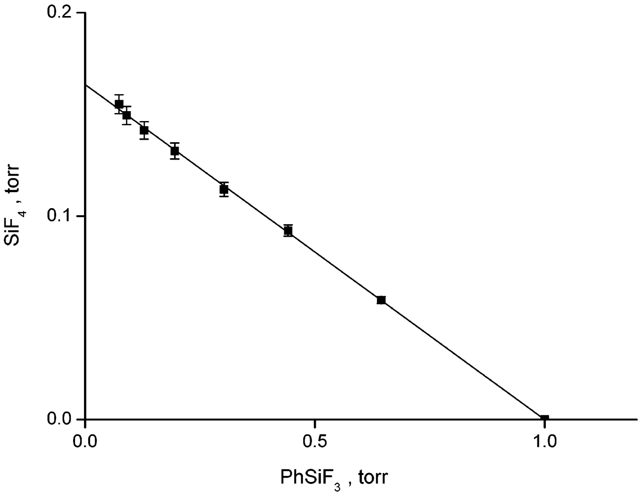

Figure 4. $PhSiF_3$ vs SiF_4 for irradiation of 1 Torr samples of neat $PhSiF_3$ at wavenumber 961 cm^{-1} and fluence 3.1 J/cm^2: (dots) experiment; (solid line) linear regression (slope = 0.164 ± 0.004).

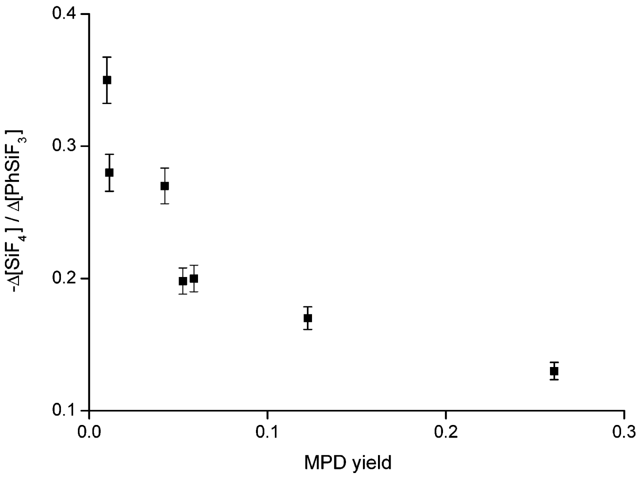

Figure 5. Number of SiF_4 molecules produced per $PhSiF_3$ molecule reacted ($-\Delta[SiF_4]/\Delta[PhSiF_3]$) versus MPD yield (irradiation of 1 Torr samples of neat $PhSiF_3$).

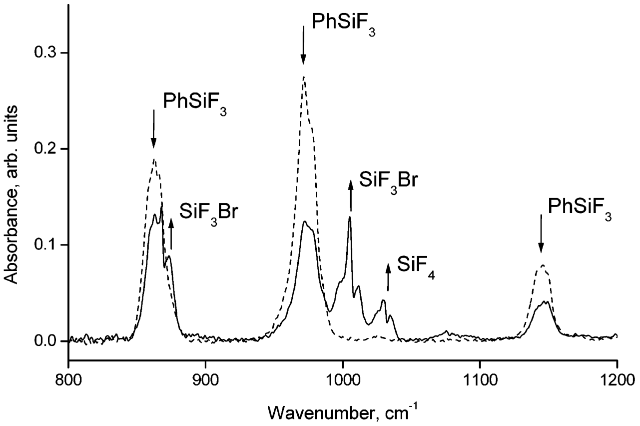

Figure 6. Change of the IR spectrum of the reaction mixture during IR MPD of $PhSiF_3$ in the presence of Br_2: (dashed line) before irradiation; (solid line) after irradiation.

is the number of SiF_4 molecules produced per $PhSiF_3$ molecule reacted. This slope depends on the MPD yield as shown in Figure 5. The dependence in Figure 5 can be explained by taking into account the following assumptions: (1) there are few channels of IR MPD of $PhSiF_3$, and (2) SiF_4 is formed by the channel with lowest activation energy. Then, if the laser fluence (and the corresponding MPD yield) is increased, the competition between the channels leads to the reduction of the number of SiF_4 molecules produced per $PhSiF_3$ molecule reacted. Additional information on the MPD channels was obtained using a scavenger (Br_2), as discussed below.

The IRMPD of $PhSiF_3$ not only yields gaseous products but also formation of a film on the windows and the inner surface of the irradiation cell is observed. The presence of these surface films on the windows could produce a reduction of the laser transmitted radiation by absorption of IR laser photons, becoming an additional source of photolysis products, as well as affecting the IR absorption measurements of $PhSiF_3$. However, control measurements did not show significant reduction of the laser radiation. The main part of the solid product precipitated in the central part of the inner surface of the cell. Besides, the formation of photoproducts by direct absorption of the film (on the windows) is negligible with respect to the reaction products obtained by laser photolysis of $PhSiF_3$.

Additional experiments on IR MPD of the mixture $PhSiF_3$ and Br_2 (as a scavenger) were carried out to establish the primary MPD products. The IR absorption spectrum before and after the irradiation is shown in Figure 6. In that case, new strong absorption peaks appeared at 873 and 1005 cm^{-1}. These new peaks were assigned to SiF_3Br (the spectrum of neat SiF_3Br is

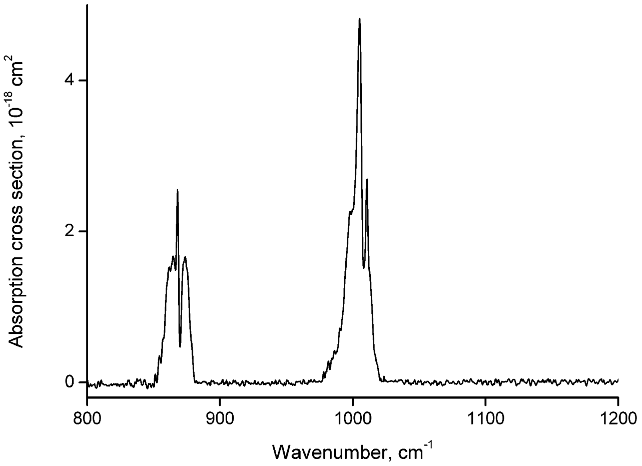

Figure 7. Measured IR absorption spectrum of neat SiF_3Br (pressure = 0.05 Torr).

shown in Figure 7). After the volatile gas products were collected at 77 K, the residual pressure was very small; i.e., the amount of H_2 was negligible. Additionally, the appearance of HBr was detected.

The proposed dissociation mechanism involves the elimination of SiF_3, channel 1, and the elimination of H, channel 2:

$$\text{channel 1:} \quad PhSiF_3 \xrightarrow{nh\nu} \dot{P}h + \dot{S}iF_3 \tag{4}$$

$$\text{channel 2:} \quad PhSiF_3 \xrightarrow{nh\nu} \dot{C}_5H_4SiF_3 + \dot{H} \tag{5}$$

The appearance of SiF_4 can be explained by the reaction

$$\dot{S}iF_3 + \dot{S}iF_3 \rightarrow \ddot{S}iF_2 + SiF_4 \tag{6}$$

Reaction 5 leads to the formation of H_2, SiF_3H, and C_6H_6. The presence of Br_2 leads to the formation of SiF_3Br by the reaction

$$\dot{S}iF_3 + Br_2 \rightarrow SiF_3Br + \dot{B}r \tag{7}$$

and the amount of H_2 created from H is negligible, due to the fast reaction of H with Br_2:

$$\dot{H} + Br_2 \rightarrow HBr + \dot{B}r \tag{8}$$

Applying the Becke3LYP DFT method and Dunning's D95-(d,p) basis set, we calculated the energy change E_1 for reaction 4 (channel 1) and E_2 for reaction 5 (channel 2): $E_1 = 106$ kcal/mol (or about the energy of 37 photons at 970 cm^{-1}) and $E_2 = 117$ kcal/mol. This compares to the energy change of 167 kcal/mol for dissociation of SiF_4 to SiF_3 and F and the energy change of 34 kcal/mol for dissociation of Si_2F_6 to SiF_4 and SiF_2[11] (in fact, Bains et al.[28] observed an activation energy of 47 kcal/mol for the reaction of Si_2F_6). The difference is a major reason that the infrared laser induces the reaction of $PhSiF_3$ easier than SiF_4, but harder than Si_2F_6. We would like to emphasize that the calculated energy change is a bit lower for the reaction 4 in comparison with the reaction 5, and therefore, the data presented in Figure 5 can be explained by the competition between the channels.

MPD yield was measured for FEL irradiation of $PhSiF_3$ at different wavenumbers in the range from 930 to 980 cm^{-1}, and the results are presented in Figure 8. The MDP yield depends strongly on the fluence, as shown in Figure 9. Approximation of the experimental data from Figure 9 by the power dependence of MPD yield Y on the fluence Φ gives the following result (for the fluence from 1.4 to 2.6 J/cm^2, and the wavenumber of 961 cm^{-1}): $Y \sim \Phi^{3.7 \pm 0.2}$. One can see from the Figure 9 that the MDP threshold for PhSiF3 is less than 0.4 J/cm^2, and the dependence "Y vs ln(Φ)" is linear in the range of the fluence from 0.4 J/cm^2 to 1 J/cm^2. The MPD theory can predict (in some approximation) the MPD yield spectrum and the dependence of Y on the fluence for a given molecule. Therefore, comparison of the theoretical prediction with the experimental data presented on Figures 8 and 9 can be used to check the applicability of the particular theoretical model of the MPD process and to develop the MPD theory further. For practical applications, the obtained experimental data on the MPD yield spectrum and the dependence of Y on the fluence can be used, for example, for optimization of an apparatus for Si isotope separation by multiphoton absorption and dissociation of $PhSiF_3$.

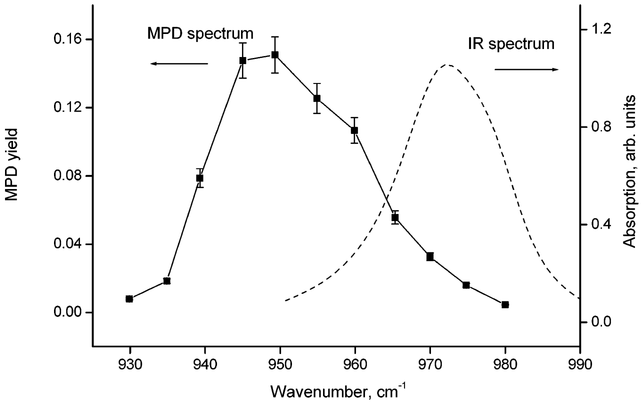

Figure 8. MPD yield spectrum (pressure = 0.25 Torr, fluence = 2.2 J/cm^2) and absorption spectrum of $PhSiF_3$.

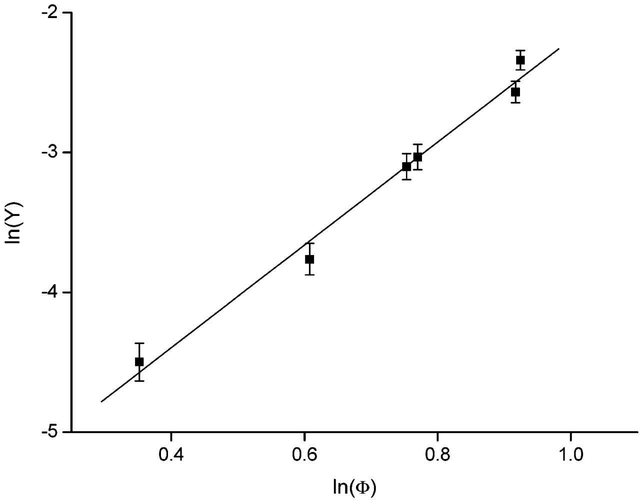

Figure 9. Dependence of ln(Y) on ln(Φ) at wavenumber 961 cm^{-1}: (dots) experimental data; (solid line) linear dependence (slope = 3.7 ± 0.2).

The dependence of the MPD yield on initial pressure $PhSiF_3$ is shown in Figure 10. The dissociation yield decreases with increasing pressure due to collisional deactivation. In our experiments the molecular excitation takes place during a macropulse, and the macropulse duration is longer than the time between collisions. Therefore, the probability decrease is caused by both (1) the relaxation of molecules during absorption and (2) the relaxation of molecules, which have absorbed energy enough for dissociation.

Isotope enrichment of $PhSiF_3$ was analyzed by a quadrupole mass spectrometer. Figure 11 shows an example of the change of the $PhSiF_3^+$ signal from the mass spectrometer after the FEL

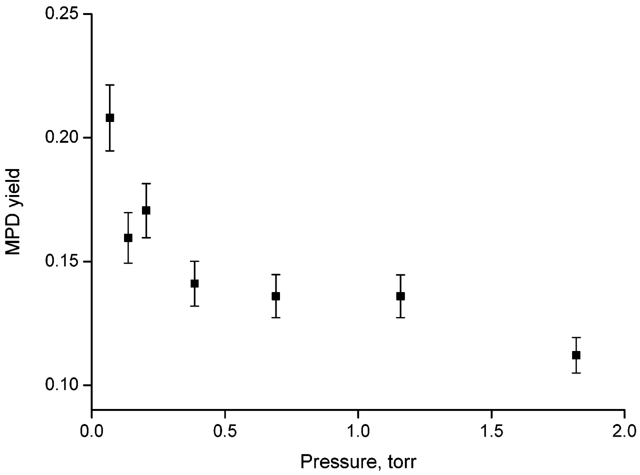

Figure 10. MPD yield vs initial pressure of $PhSiF_3$ (wavenumber = 961 cm^{-1}, fluence = 2.5 J/cm^2).

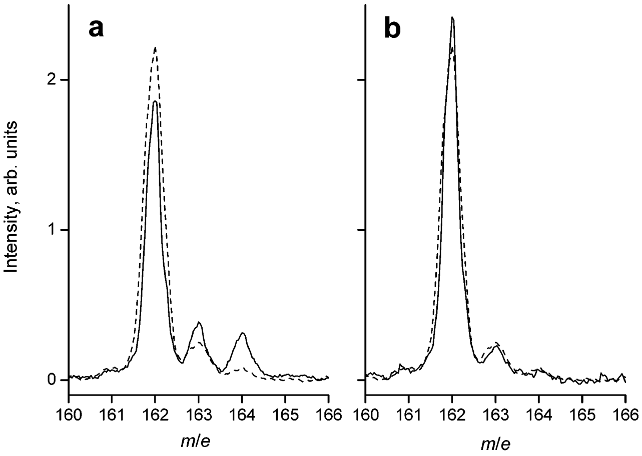

Figure 11. Example of mass spectra before (dashed line) and after (solid line) the FEL irradiation (fluence = 3.1 J/cm^2, irradiation time = 380 min) at different wavenumbers: (a) 961 cm^{-1}; (b) 934 cm^{-1}. The spectra were normalized to the same total intensity of all three peaks.

TABLE 2: Isotopic Selectivities S_{ij} at 1 Torr and Different Wavenumbers

	961 cm^{-1}	925 cm^{-1}
$S_{29,28}$	0.65 ± 0.06	2.5 ± 0.2
$S_{30,28}$	0.44 ± 0.04	2.3 ± 0.2

irradiation (mass spectra were normalized to demonstrate the change of the isotope ratio). It was shown that after the irradiation of neat $PhSiF_3$ (initial pressure 1 Torr) for 6 h at wavenumber 961 cm^{-1} and fluence 2.5 J/cm^2, the abundance of ^{28}Si in $PhSiF_3$ decreased from 92.2 ± 0.9 to 77.1 ± 0.7%, and the abundance of ^{30}Si increased from 3.10 ± 0.03 to 12.3 ± 0.1% (Figure 11a). After the irradiation of neat PhSiF3 at wavenumber 925 cm^{-1} (and the same other conditions), the abundance of ^{30}Si in $PhSiF_3$ decreased from 3.10 ± 0.03 to 1.50 ± 0.02%, and the abundance of ^{28}Si increased from 92.2 ± 0.9 to 96.5 ± 0.9% (Figure 11b). The isotopic selectivities were estimated from these experiments, and the results are shown in Table 2. These values are less than the reported isotopic selectivities for IR MPD of Si_2F_6. We suggest two main reasons for that (1) the longer and broader FEL pulse and (2) the batch operation. It is well-known[11] that the batch mode operation reduces substantially the isotopic selectivity in comparison with the flow system. On the other hand, the spectral width of the FEL radiation in our experiments was ~7 cm^{-1} (0.7% near 1000 cm^{-1}), which is about the same value as the isotopic shift (~8 cm^{-1}). In such conditions, the isotopic selectivity is not expected to be high. The possibility to reach high isotopic selectivity under improved conditions is an argument for additional research on LIS of $PhSiF_3$.

Conclusions

In this work, the infrared FEL induced isotopically selective multiphoton dissociation of $PhSiF_3$ molecules in the gaseous phase. By using the scavenger Br_2, it was established that the first products of multiphoton dissociation of $PhSiF_3$ are SiF_3 and Ph radicals (channel 1) and $C_5H_4SiF_3$ and H radicals (channel 2). The isotopic selectivity for the LIS of $PhSiF_3$ is not as high as the reported selectivity for Si_2F_6. The longer and broader FEL pulse is partially responsible for the lower selectivity. Another reason could be that the FEL experiments with $PhSiF_3$ were performed in a batch mode.

In our future work we are planning to continue investigation of the reaction pathways initiated by IR multiphoton dissociation of $PhSiF_3$. Detailed knowledge of the mechanism of the conversion of $PhSiF_3$ to SiF_4 is important for optimization of the process of Si isotope separation. Generally, the efficiency of laser isotope separation can be increased in different ways: (1) decreasing the pressure of the gaseous mixture; (2) reducing the spectral width of the FEL radiation; (3) increasing the FEL macropulse energy, etc. Another way is to find a chemical that provides only molecular products as a primary result of IR MPD. For example, in the case of carbon isotopes separation, the chemical was found, that is, formic acid.[5] Molecules (not radicals) are the primary products of IR MPD of formic acid molecules in gaseous phase under the action of FEL radiation. It would be very interesting to find such a chemical for Si isotope separation as well.

Acknowledgment. The studies described here were supported by the following grants: the Grant-in-Aid for the Creative Scientific Research of Japan Society for the Promotion of Science (No. 11NP0101); the Grant of Russian Fund of Basic Research (No. 01-03-40101); the Grant of Siberian Division of Russian Academy of Science (No. 86-2001).

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