Enrichment of Silicon Isotopes with Infrared Free-Electron Laser Radiation

John L. Lyman* and Brian E. Newnam†
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Tetsuji Noda‡ and Hiroshi Suzuki§
National Research Institute for Metals (NRIM), 1-2-1, Sengen, Tsukuba, Ibaraki 305, Japan

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We have used the FELIX infrared free-electron laser (FEL) at the FOM Institute for Plasma Physics in The Netherlands to enrich silicon isotopes by multiple-photon dissociation of the molecule Si_2F_6. The absorption of infrared radiation induces the reaction $Si_2F_6 \rightarrow SiF_4 + SiF_2$. Much of the SiF_2 product further reacts to form additional SiF_4. The Si_2F_6 molecule has absorption bands in the 10, 12, and 25 μm spectral regions. FEL-induced reactions occurred in all three regions. The reaction fraction was highest for the stronger band in the 10 μm region. Reactions in all three bands were isotopically selective. Irradiation in the 10 μm region at 952 cm^{-1} gave an isotopic selectivity of 5.6 for ^{30}Si. For comparison, the published isotopic selectivity using a CO_2 laser in the same spectral region is in excess of 17. We attribute the lower selectivity obtained with an FEL to its longer macropulse, its broader spectral width, and differences in experimental procedure. FEL irradiation in the region of the 12 μm band produced isotopic selectivities in excess of 20 for ^{30}Si. Selective production of ^{28}Si was high in the 25 μm region. We used changes in the infrared spectra of the irradiated samples for all analyses of reaction and isotope enrichment except for a single confirmation of enrichment with a mass spectrometer.

Introduction

Silicon isotopes have been enriched by reactions induced with infrared lasers.[1−5] Except for the earliest demonstration,[5] which was infrared dissociation of SiF_4, all of the recent work has been with the species Si_2F_6. In all previous cases, the infrared source has been the carbon dioxide laser. A free-electron laser (FEL) has some potential advantages (as well as disadvantages) for isotope separation. The most obvious advantage is that many infrared frequencies are accessible, since FELs are continuously tunable over a broad frequency range. On the other hand, the possibility exists that the FEL's broader frequency width or long macropulses may degrade the isotopic selectivity of a photo-induced chemical reaction. In this paper we report our study of the isotopically selective reaction of Si_2F_6 induced with an infrared FEL. Our experiments were performed in the FELIX facility at the FOM Institute for Plasma Physics in The Netherlands.

The Si_2F_6 molecule has three strong infrared absorption features.[6,7] They are at 10 μm (ν_7), 12 μm (ν_5), and 25 μm (ν_6). We performed infrared multiple-photon dissociation experiments in all three spectral regions. The induced reactions were isotopically selective in all three regions. Silicon has three stable isotopes:[8] ^{28}Si (92.23%), ^{29}Si (4.67%), and ^{30}Si (3.10%).

The first demonstrations of infrared photochemistry by multiple-photon dissociation with an infrared FEL[9,10] involved $CFCl_3$ and CF_2Cl_2. The experiments showed that FEL radiation effectively induces chemical reactions. Isotopically selective multiple-photon dissociation with an FEL was a logical next step. Because of a variety of potential applications for isotopically pure silicon[1−4] and because of our previous photochemical experience[4] with Si_2F_6, we chose to conduct FEL isotope separation experiments with that species. Other research groups have determined that multiple-photon dissociation with an infrared FEL can be isotopically selective, resulting in significant enrichment of carbon[11−17] and nitrogen[18] isotopes.

Experimental Procedure

The Si_2F_6 used in these experiments was synthesized and purified previously at the National Research Institute for Metals (NRIM) and shipped to the FELIX facility in The Netherlands. The only detectable impurity in the sample was ∼0.5% SiF_4, as determined from the infrared spectrum of Si_2F_6. That species was a product of the laser-induced reaction, thermal reaction, and reaction with water. No additional purification of the Si_2F_6 was conducted.

We performed the experiments by irradiating samples of Si_2F_6 with laser pulses from the FELIX facility. The irradiation was performed in two stainless steel cells used in our previous FEL photolysis experiments.[10] The optical path length within the cells was 75 mm, and the internal diameter was 10 mm. KCl windows were used for one cell and CsI windows for the second cell, the latter being essential for transmitting FEL radiation in the 25 μm spectral region.

A typical experimental procedure follows. (1) Evacuate the reaction cell. (2) Take an infrared spectrum of the empty cell. (3) Fill the cell to 0.039 kPa of Si_2F_6. (4) Take an infrared spectrum of the filled cell. (5) Select the laser wavelength. (6) Measure the laser pulse energy at the point of irradiation. (7) Irradiate the sample at 5 Hz repetition rate for a specified time. (8) Take an infrared spectrum of the irradiated sample. No diluent or scavenger gases were used in these tests.

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* To whom correspondence should be addressed. E-mail: lyman@lanl.gov.
† E-mail: bnewnam@lanl.gov.
‡ E-mail: noda@nrim.go.jp.
§ E-mail: suzuki@momokusa.nrim.go.jp.

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We measured the temporal, frequency, and spatial profiles of the FEL beam used for irradiation. The 4 μs macropulse consisted of a series of micropulses ~5 ps (fwhm) separated by 1 ns. The picosecond micro-pulse-length was the main contributor to the frequency width of 0.5% used in all experiments. Its spatial profile had radial symmetry and was near-Gaussian within the test cells. The laser fluence varied with radius as

$$\Phi = \frac{E}{a^2\pi}\exp[-(r/a)^2] \tag{1}$$

where E was the measured pulse energy, $a = 1.15$ mm was the beam radius, and r was the distance from the center of the beam. With reference to similar enrichment experiments we conducted with a CO_2 laser,[4] the 4 μs FEL macropulse was about an order of magnitude longer, the FEL frequency width was several orders of magnitude greater, and the FEL laser fluence was comparable. With the CO_2 laser, Suzuki et al.[4] found ~0.4 J/cm^2 to be the laser fluence for optimum isotope separation in the region of the 10 μm band of Si_2F_6. The FEL experiments were conducted at a similar fluence. The corresponding average pulse energy for the FEL experiments in the 10 μm spectral region was 23.2 mJ. The resulting fluence at the beam center was 0.558 J/cm^2, and at the inflection points ($a = 1.15$ mm) it was 0.205 J/cm^2. The corresponding average fluence was

$$\bar{\Phi} = E/(2\pi a^2) = 0.279 \text{ J/cm}^2 \tag{2}$$

Analytical Procedures

Transmittance of the gas cell, before and after FEL irradiation, was performed with a Nicolet Fourier transform infrared spectrometer. Analysis of the data enabled determinations of the amount of the Si_2F_6 reacting in each experiment, the amount of SiF_4 produced in each experiment, and the isotopic distribution in the SiF_4 reaction product. Beer's law was assumed to be valid for the experimental conditions, from which the absorbance of an absorption feature was proportional to the partial pressure of the species responsible for that feature. We determined the change in the amount of Si_2F_6 from the change in absorbance at the peak of the 12 μm R-branch of Si_2F_6 (826.7 cm^{-1}) and the change in the amount of SiF_4 from the absorbance change at the SiF_4 ν_3 R-branch at 1034.6 cm^{-1}. Previous analysis[19] of the infrared spectrum of the SiF_4 allowed us to identify the strong Q-branch of the ν_3 absorption band for each of the three silicon isotopic forms of this molecule. Because the Q-branches are all overlapped by other features of the ν_3 band, it was necessary to carefully define the baseline for peaks by drawing straight lines through other features of the spectrum. We chose the lines to give the correct isotopic distribution for a standard SiF_4 spectrum, which we recorded earlier. Identical procedures were used for all isotope analyses of the SiF_4 reaction product.

Laser-Induced Reaction of Si_2F_6

As described above, the FEL experiments involved irradiation of a cell containing a sample of Si_2F_6 a number of times before checking the extent of the reaction. From those multiple-pulse experiments we were able to derive the fraction of the irradiated molecules reacted per pulse. We followed earlier work[20] for expressions for reaction fraction and isotopic selectivity. With the assumption that the amount of Si_2F_6 reaction induced by the laser depends only on the amount of Si_2F_6 currently present, we get f, the fraction of irradiated molecules reacting per pulse:

$$f = -\frac{V_{\text{cell}}}{V_{\text{irr}}}\frac{\ln f_r}{i} \tag{3}$$

where

$$f_r = [Si_2F_6]/[Si_2F_6]_0 \tag{4}$$

is the fraction of reactant remaining in the cell after the experiment, V_{cell} (3200 mm^3) is the cell volume, V_{irr} (312 mm^3) is the irradiated volume enclosed by the beam radius a in eq 1, $[Si_2F_6]$ is the final concentration, $[Si_2F_6]_0$ is the initial concentration, and i is the number of laser pulses. Because of the method of analysis, the quantity f was very nearly f_{28}, the fraction of silicon-28 isotope that reacted. With the concentration of the reactant before and after irradiation, the volumes described above, and the number of laser pulses, we have the quantity f for a particular set of experimental conditions.

We describe the isotope enrichment factor, β_m, for isotope m as

$$\beta_m = R_m/R_m^{\ 0} \tag{5}$$

where R_m is the fraction of isotope m in the SiF_4 product after irradiation, and R_m^0 is the natural fraction of silicon isotope m.

We express the isotopic selectivity (α_m) of the laser-induced reaction of isotope m relative to isotope 28 as the ratio of f_m to f_{28}. In terms of β_m,

$$\alpha_m = f_m/f_{28} = \ln[1 + \beta_m(1 - f_r)]/\ln[1 + \beta_{28}(1 - f_r)] \tag{6}$$

Correction for Reaction without Laser Irradiation

All experiments were performed with two cells. One of these, cell A, had KCl windows. The other, cell F, had CsI windows. We found that the Si_2F_6 reacted spontaneously in both cells to produce SiF_4. This interfered with both our analysis of the measurement of the extent of the laser-induced reaction and with the isotopic composition of the SiF_4 product. The reaction was probably on the cell surface with possible contribution from water in the cell. We measured the rate of this spontaneous reaction in the two cells. The spontaneous reaction rate in cell A decayed exponentially from 2.2% per minute initially to 0.3% per minute at 1.5 h. The spontaneous reaction rate in cell F was faster. It decayed exponentially from 8% per minute initially to 1% per minute at 8 h. We used these measurements to correct reaction yield for this spontaneous reaction. However, none of the measured isotopic selectivities were corrected for the spontaneous reaction. This correction would have increased the reported selectivities.

Thermochemistry and Reaction Mechanism

The infrared spectrum before and after irradiation provided quantitative measures of the amount of SiF_4 produced and the amount of Si_2F_6 reacted in each experiment. Figure 1 shows an example of the amount of SiF_4 produced versus the amount of Si_2F_6 reacted in experiments at 12 μm. The slope (1.41 ± 0.04) of the fit to those points is the number of SiF_4 molecules produced per Si_2F_6 molecule reacted. Similar experiments in the region of the 10 μm band gave a slope of 1.30 ± 0.06. Experiments in the 25 μm region produced a lower slope, 1.02 ± 0.09. In the latter case, however, the irradiation time was longer and the number of experiments was fewer. The results of these experiments indicate that a reasonable reaction mechanism is

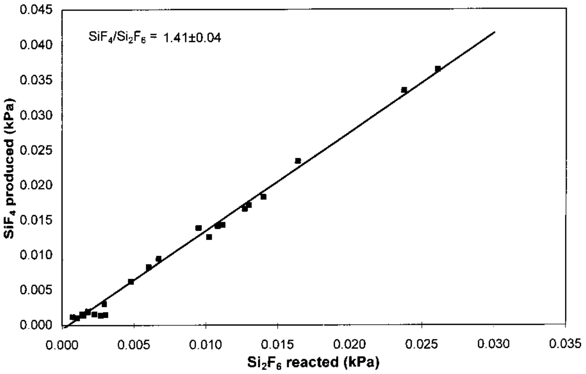

Figure 1. SiF_4 produced vs Si_2F_6 reacted for irradiation of 0.039 kPa samples of Si_2F_6 at various frequencies in the 12 μm band.

$$Si_2F_6 \Rightarrow SiF_4 + SiF_2 \tag{7}$$

followed by some fraction of the product reacting, probably at a surface, as

$$SiF_2 + SiF_2 \Rightarrow SiF_4 + Si_s \tag{8}$$

where Si_s is solid silicon. These reactions give a ratio of 1.5 for SiF_4 produced to Si_2F_6 reacted. Because the measured ratio was less than that value for all three sets of experiments, some fraction of the fluorine atoms in reaction 8 remained in the solid polymeric material. Earlier experiments by Lampe and Biedrzycki[21] showed that reaction 7 is the initial infrared photochemical reaction.

The spread of the points about the straight line in Figure 1 is also an indication of the precision of the measurement of molecular density from the FTIR spectra. The average vertical deviation from the line is 0.0019, or about 5% of the maximum value of SiF_4.

The enthalpy change[22] for reaction 7 is low, $\Delta H°(298) = 141.2$ kJ/mol, or about the energy of 12 photons at 970 cm^{-1}. This compares to an enthalpy change of 700.7 kJ/mol, or about the energy of 60 photons at 970 cm^{-1}, for dissociation of SiF_4 to SiF_3 and F. The difference is a major reason that the infrared laser induces the reaction of Si_2F_6 so easily. Because of the complexity of the reaction of Si_2F_6 compared to a simple dissociation reaction, the energy barrier for reaction will exceed the enthalpy change by some amount. In fact, Bains et al.[23] observed an activation energy of 193.5 kJ/mol for reaction 7, or about 17 photons at 970 cm^{-1}.

Reaction in the 10 μm Band

FEL irradiation in the region of the 10 μm ($\nu_7^{6,7}$) band of Si_2F_6 induces reaction of the molecule. Figure 2 shows the fraction of irradiated molecules reacting per laser pulse, *f*, over the wavelength range in the 10 μm region with and without correction for the spontaneous reaction. The resulting set of points is the reaction spectrum. The figure also shows the absorption spectrum in that wavelength region taken for the sample with the FTIR spectrometer. The average pulse energy for all points in the experiment was 23.2 ± 0.7 mJ/pulse. This is a 3% average deviation for all of the experiments in Figure 2 and an average fluence of 0.28 J/cm^2. This reaction spectrum has a shape similar to that of the infrared absorption band shown in the figure, but it is shifted by 12.5 cm^{-1} to lower wavenumber. Near the peak of the reaction spectrum nearly half of the molecules in the irradiated region reacted. All of the previous laser photolysis experiments[1-4] with this molecule have been performed in the region of this absorption band with a CO_2 laser.

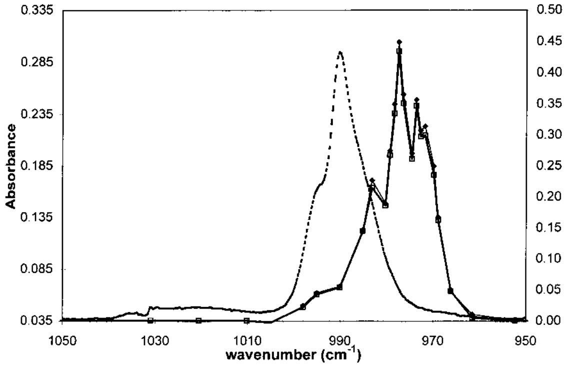

Figure 2. Infrared spectrum (dashed line, left axis) and reaction spectrum (right axis) for 0.039 kPa of Si_2F_6 irradiated in the region of the 10 μm absorption band. The diamonds are the uncorrected fraction reacted per pulse, and the open squares are the same points corrected for the spontaneous reaction.

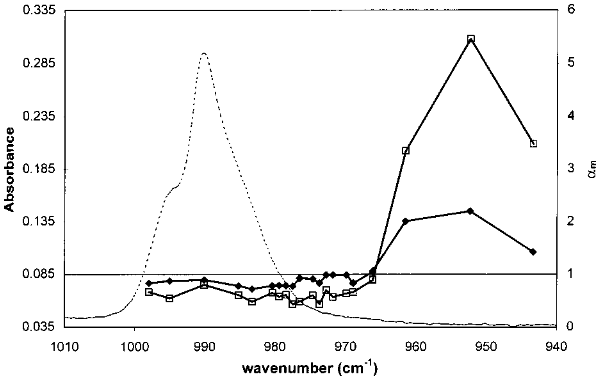

Figure 3. Isotopic selectivity (right axis, eq 6) for reaction of Si_2F_6 in the region of the 10 μm absorption band. The diamonds are for α_{29}, and open squares are for α_{30}. The dashed line is the infrared spectrum (left axis), and the horizontal line is at 1.0 on the α_m scale.

The steep slope on the low-frequency side of the reaction spectrum (Figure 2) indicates that the isotopic selectivity of the reaction should be high for reaction of the heavier isotopic forms of the molecule. Our experimental measurements show that this is so. Figure 3 shows the isotopic selectivity (α_m) for each of the minor isotopes. From the definition of α_m (eq 6) we see that the species $^{28}SiF_4$ was produced preferentially above 977 cm^{-1}. (α_{29} and α_{30} are both less than 1.0.) At wavenumbers slightly below 977 cm^{-1} α_{29} approaches 1.0, which indicates that $^{29}SiF_4$ is more likely to be produced. At still lower wavenumber, below 965 cm^{-1}, α_m was high for each minor isotope. We note that the selectivity for ^{30}Si was as high as 5.6 at 952 cm^{-1}.

Because some questions may exist about the efficacy of the FTIR spectra for determining isotope enrichment, we performed one experiment where we irradiated flowing Si_2F_6 gas with the FEL at 950 cm^{-1}. We attempted to reproduce the procedures of ref 4. First, we collected the irradiated sample cryogenically in a liquid nitrogen trap. We then separated the Si_2F_6 from the SiF_4 by trapping the Si_2F_6 with an ethanol slurry. We then shipped the SiF_4 back to NRIM in Japan and measured the isotope ratios with the mass spectrometer described in ref 4. We obtained the following enrichment factors:

$$\beta_{28} = 0.98$$

$$\beta_{29} = 1.02$$

and

$$\beta_{30} = 1.54$$

Because of the nature of the experiments, we did not obtain a value of the fraction reacted. Consequently, we did not obtain a precise value of the isotopic selectivity (eq 6) for these measurements. We do know, however, that the fraction reacted was small. From eq 6, α_m approaches β_m/β_{28} in the limit of the small fraction reacted.

The conditions for these experiments were quite different from those of Figure 2. The fraction of the flowing Si_2F_6 irradiated was small, and the laser fluence was higher by about a factor of 2. Because of the small fraction irradiated, much of the SiF_4 trapped was the 0.5% impurity present in the Si_2F_6 sample. The enrichment factors, particularly β_{30}, do show that the FTIR procedure is appropriate.

Reaction in the 12 μm Band

As in the case of irradiation in the 10 μm band, irradiation with the FEL near 12 μm (ν_5^{6,7}) also induced reaction. The infrared absorption band was weaker, however, and so the amount of reaction was less. Figure 4 shows the reaction spectrum and the FTIR spectrum in the 12 μm region. The average pulse energy was 19.6 ± 0.9 mJ/pulse. This is a 5% deviation for the experiments in Figure 4 and an average fluence of 0.24 J/cm^2. This pulse energy was about 85% of that used in the 10 μm experiments. The reaction is again similar in shape to the FTIR spectrum but was shifted by ~8 cm^{-1} to lower wavenumber, which is somewhat less than the 12.5 cm^{-1} shift in the 10 μm experiments.

FEL irradiation in this band is also isotopically selective. Figure 5 shows the isotopic selectivity for the two minor isotopes, as well as the FTIR spectrum of the band. In the region of low fraction reacted (below 810 cm^{-1}) the isotopic selectivity was high for the minor isotopes. In fact, it was even greater than for the low-frequency side of the 10 μm band.

Reaction in the 25 μm Band

Experiments in the region of the 25 μm (ν_6^{6,7}) band were complicated by several problems. One of these was that it was necessary to use CsI windows to reach that wavelength range. As we noted above, the Si_2F_6 gas reacts spontaneously much more rapidly in the cell with CsI windows than in the cell with KCl windows. The laser pulse energy was also less stable than in the region of the other two bands. We irradiated the samples with either 120 or 300 pulses but only used the data for 300 pulses because of interference with the analysis from spontaneous reaction when we used fewer pulses. Consequently, the range of frequencies was less than we wanted. Nevertheless, we did show reaction when the Si_2F_6 was irradiated in the 25 μm band. Figure 6 shows the results of those experiments. The fraction reacted was about the same as that from irradiation in the 12 μm band, but we do not see the shift to longer wavelength that we saw in the other two bands. The peak of the reaction spectrum is very near the center of the absorption band. The average pulse energy for all points in the experiment was 23.5 ± 1.7 mJ/pulse. This is an average fluence of 0.282 J/cm^2 and a 7% average deviation.

Because of the problems mentioned above, the isotope enrichment results are minimal. As evident in Figure 7, we did get very low isotopic selectivity for production of the two minor isotopes. This indicates a high probability for production of $^{28}SiF_4$ by irradiation of Si_2F_6 at the center of the 25 μm absorption band. Irradiation in this band appears to be best for selective reaction of $^{28-28}Si_2F_6$. Note that α_{30} has a lower value in the 25 μm band than in either of the other two bands (Figures 3 and 5).

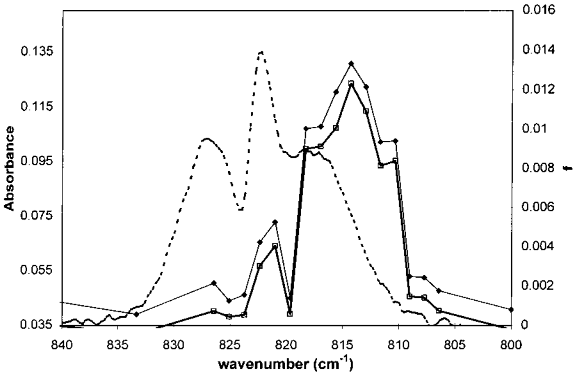

Figure 4. Infrared spectrum (dashed line) and reaction spectrum of Si_2F_6 for irradiation in the region of the 12 μm absorption band. The diamonds are the uncorrected fraction reacted per pulse, and the open squares are the same points corrected for the spontaneous reaction.

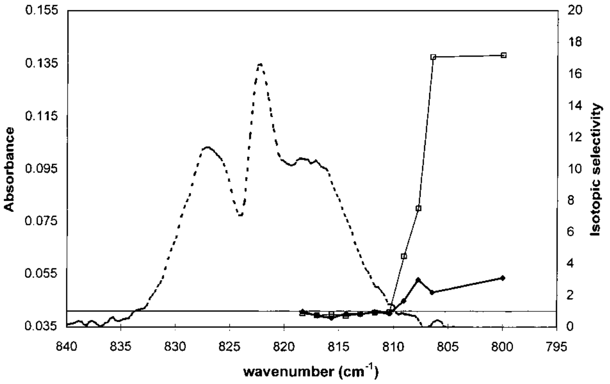

Figure 5. Isotopic selectivity (eq 6) for reaction of Si_2F_6 in the region of the 12 μm absorption band. The diamonds are α_{29}, and open squares are α_{30}. The dashed line is the infrared spectrum, and the horizontal line is at 1.0 on the α_m scale.

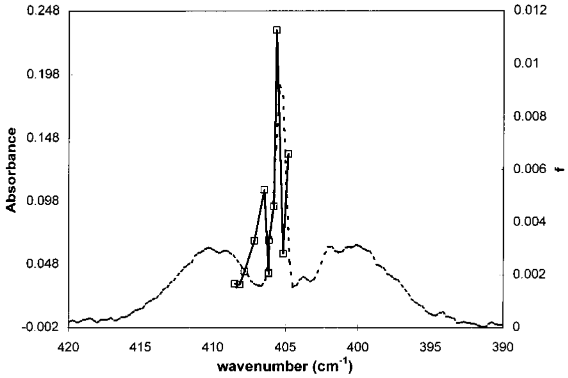

Figure 6. Infrared spectrum (dashed line) and reaction spectrum of Si_2F_6 (open squares) for irradiation in the 25 μm region. The reaction spectrum is corrected for the spontaneous reaction.

Comparison of FEL Enrichment with CO_2 Laser Enrichment

Many silicon isotope separation experiments have been done with the CO_2 laser. The results, however, have not been reported as isotopic selectivity, α_m, as in eq 6. The data in Figures 3 and 5 of ref 4, however, give sufficient information to calculate the isotopic selectivity by eq 6. Figure 8 shows that comparison. The FEL data are those in Figure 3, and the CO_2 laser data are

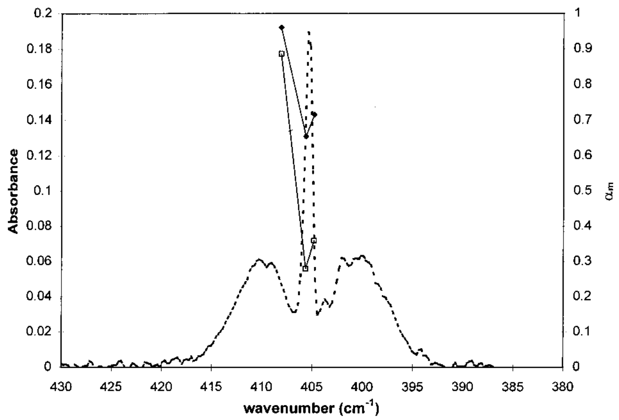

Figure 7. Infrared spectrum and isotopic selectivity for reaction of Si_2F_6 for irradiation in the 25 μm region. The diamonds are α_{29}, and open squares are α_{30}.

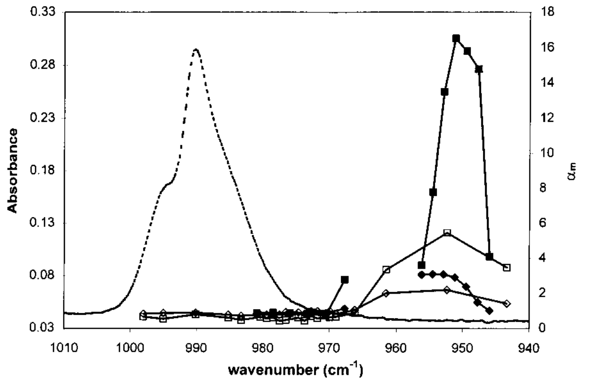

Figure 8. Comparison of the isotopic selectivity for reaction of Si_2F_6 induced by the FEL (open points) and by a CO_2 laser (filled points) in the 10 μm region. The diamonds are α_{29}, and squares are α_{30}. The CO_2 laser points were calculated from eq 6 using data from ref 4. The dashed line is the infrared spectrum.

from ref 4. We see that the selectivities are qualitatively similar. However, in the region of 950 cm^{-1}, the selectivities with the CO_2 laser exceed those we obtained with the FEL.

We conclude from this comparison that FEL radiation is not as selective as the CO_2 laser. This comparison is only for the region of the ν_7 band. The indications of Figures 5 and 7 are that the FEL isotopic selectivity for the ν_5 (12 μm) band and the ν_6 (25 μm) band exceeds that of the ν_7 (10 μm) band. We mentioned in the Introduction that the FEL radiation might be less selective for two reasons. The first of these is the much greater spectral width, and the second is the longer laser macropulse. Both of these probably contribute to the lower selectivity with the FEL. The higher FEL isotopic selectivity in the longer wavelength bands, however, may be due to the fact that those bands are weaker. This reduces laser absorption and the extent of reaction. We see from Figures 2, 4, and 6 that the peak absorbance for the 12 μm band was about half that for the 10 μm band and the peak absorbance for the 25 μm band was about two-thirds that for the 10 μm band. The peak fraction reacted per pulse for the longer-wavelength bands was, however, 3% of the fraction reacted per pulse for the 10 μm band. The lower reaction fraction could give a higher selectivity because of less thermal reaction.

We suggest another reason for the difference between the isotopic selectivity with the FEL and with the CO_2 laser. In earlier work we found that in our experiments using the CO_2 laser[4] a flowing system was very important for silicon isotope separation. When we used a batch system, such as the method used in the current FEL experiments, the isotope enrichment was very low. We do not know if the lower selectivity under FEL irradiation is due to the characteristics of FEL beam or to the batch operation. We intend to resolve this question in future experiments by repeating the FEL experiments with a flow system.

A higher isotopic selectivity for the 12 μm band was unexpected because the isotope shift for that band is lower than for the 10 μm band. The infrared spectral isotope shift between $^{28-28}Si_2F_6$ and $^{28,29}Si_2F_6$ is 3.9 cm^{-1} for the 10 μm band.[7] For the 12 μm band[7] it is a lower value of 1.6 cm^{-1}. The isotope shift for the 25 μm band was not reported in ref 7, but we see from the infrared spectrum in Figure 6 that two apparent isotopic Q-branches are just to the right of the main Q-branch for $^{28-28}Si_2F_6$. The intensities, inferred from the isotope ratios,[8] are just about right to be those for $^{28,29}Si_2F_6$ and $^{28-30}Si_2F_6$. From this spectrum we infer that the isotope shift between $^{28-28}Si_2F_6$ and $^{28,29}Si_2F_6$ is 1.9 cm^{-1} for the 25 μm band. Even though the isotope shifts are smaller for the two longer-wavelength bands, they are sufficient for isotope separation in these spectral regions.

Conclusions

The infrared FEL induced an isotopically selective reaction in three absorption bands of the Si_2F_6 molecule. The reaction appears to be one that produces one molecule of SiF_4 and one of SiF_2. Subsequent reactions of the SiF_2 produce additional SiF_4.

The reaction spectrum in the region of the three bands has a shape similar to the shape in small-signal infrared absorption spectra. For the 10 and 12 μm bands, however, the reaction spectrum is shifted to longer wavelengths. The reaction spectrum in the 25 μm region does not appear to have that shift. This is likely due to the lower anharmonicity of the 25 μm bending vibration.

The isotopic selectivity for the FEL reactions is not as high as that for CO_2 laser irradiation. The longer and broader FEL pulse is partially responsible for the lower selectivity. Another reason could be that the FEL experiments were performed in a batch mode while the CO_2 laser experiments were performed under flow conditions. Batch-mode experiments with the CO_2 laser produced no enrichment. The higher isotopic selectivity for the longer-wavelength bands is an argument for additional research on FEL isotope separation.

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References and Notes

(1) Kamioka, M.; Ishikawa, Y.; Arai, S.; Isomura, S.; Takamiya, N. *Laser Sci. Prog. Rep. IPCR* **1985**, *7,* 57.

(2) Okamura, H.; Tosa, V.; Takeuchi, K. *Jpn. J. Appl. Phys., Part 2* **1995**, *34,* L1497.

(3) Okada, Y.; Takeuchi, K. *Laser Sci. Prog. Rep. IPCR* **1996**, *18,* 74.

(4) Suzuki, H.; Araki, H.; Noda, T. *J. Jpn. Inst. Met.* **1997**, *61,* 145.

(5) Lyman, J. L.; Rockwood, S. D. *J. Appl. Phys.* **1976**, *47,* 595.

(6) Tosa, V.; Isomura, S.; Kuga, Y.; Takeuchi, K. *Vib. Spectrosc.* **1994**, *29*, 631.

(7) Tosa, V.; Ashimine, K.; Takeuchi, K. *J. Mol. Struct.* **1997**, *410−411*, 411.

(8) *CRC Handbook of Chemistry and Physics*, 69th ed.; Weast, R. C., Ed.; The Chemical Rubber Co.: Boca Raton, Fla., 1989; p B-321.

(9) Newnam, B. E.; Early, J. W.; Lyman, J. L. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1994**, *341*, 142.

(10) Lyman, J. L.; Newnam, B. E.; Early, J. W.; van der Meer, A. F. G. *J. Phys. Chem. A* **1997**, *101*, 49.

(11) Petrov, A. K.; Chesnokov, E. N.; Gorelik, S. R.; Molin, Yu. N.; Straub, K. D.; Meidin, D. M. D.; Sharmes, E. B. *Dokl. Akad. Nauk* **1997**, *352*, 774.

(12) Petrov, A. K.; Chesnokov, E. N.; Gorelik, S. R.; Straub, K. D.; Szarmes, E.; Madey, J. M. J. *J. Korean Phys. Soc.* **1997**, *30*, 364.

(13) Petrov, A. K.; Chesnokov, E. N.; Gorelik, S. R.; Straub, K. D.; Szarmes, E. B.; Madey, J. M. J. *J. Phys. Chem. A* **1997,** *101*, 7200.

(14) Kuribayashi, S.; Tomimasu, T.; Kawanishi, S.; Arai, S. *Rev. Laser Eng.* **1997**, *25*, 864.

(15) Nagai, A.; Tomimasu, T. *J. Jpn. Soc. Infrared Sci. Technol.* **1997**, *7*, 45.

(16) Arai, S.; Ikawa, K.; Matsumoto, Y.; Iizuka, Y.; Sugita, K.; Sarkar, S. K.; Kuribayashi, S. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1998**, *144*, 193.

(17) Kuribayashi, S.; Tomimasu, T.; Kawanishi, S.; Arai, S. *Appl. Phys. B* **1997**, *B65*, 393−398.

(18) Petrov, A. K.; Chesnokov, E. N.; Gorelik, S. R.; Straub, K. D.; Szarmes, E. B.; Madey, J. M. J. *Russ. Chem. Bull.* **1998**, *47*, 719.

(19) McDowell, R. S.; Reisfeld, M. J.; Patterson, C. W.; Krohn, B. J.; Vasquez, M. C.; Laguna, G. A. *J. Chem. Phys.* **1982**, *77*, 4337.

(20) Lyman, J. L.; Rockwood, S. D.; Freund, S. M. *J. Chem. Phys.* **1977**, *67*, 4545.

(21) Lampe, F. W.; Biedrzycki, J. *Spectrochim. Acta, Part A* **1990**, *46A*, 631.

(22) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1990**, *94*, 5120.

(23) Bains, S. K.; Noble, P. N.; Walsh, R. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 837.