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Infrared Multi-Photon Dissociation of SiF_3I by Co-Irradiation with FEL and TEA-CO_2 Laser

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IR multi-photon dissociation of SiF_3I in gaseous phase (pure SiF_3I at 5 torr with natural abundance of Si isotopes) was studied by use of the mid-infrared free electron laser (MIR-FEL) of the IR FEL Research Center of the Tokyo University of Science. The following three kinds of experiment were carried out: irradiation with FEL only, irradiation with TEA-CO_2 laser and co-irradiation with FEL and TEA-CO_2 laser. Upon irradiating SiF_3I with a strong light in the 10 μm spectral region, SiF_3I was partially dissociated. The dissociation rate was found to be markedly enhanced by the co-irradiation with TEA-CO_2 laser and FEL. The experimental results showed that the dissociation reaction $SiF_3I \rightarrow SiF_3 + I$ was induced by the multi-photon process, but isotope selectivity could not be found because SiF_3 radical thus formed further reacted to form SiF_4, SiF_3I and SiF_2I_2.

KEYWORD: free electron laser, multi-photon dissociation, silicon, isotope separation

1. Introduction

Recently there appears a great interest in the isotopically-pure silicon from the viewpoint of electronic industries. For instance, ^{30}Si is used for NTD (Neutron Trans-mutation Doping) to produce homogenous n-type silicon semiconductors, which is important for power semiconductor applications. Highly enriched silicon isotope is required to provide a material with enhanced optical, electr[illegible]d/or heat dissipation characteristics useful for improved microelectronics.

These demands have stimulated the investigation on the isotope separation process for Si. Laser isotope separation (LIS) process seems to be most promising because of its high isotope selectivity. In the study of LIS, TEA-CO_2 laser is usually used as the stimulating light source. However the tunability of TEA-CO_2 laser is too small for the purpose to carry out a systematic exploration of the most appropriate working material. In this sense, FEL is expected to be a very useful tool in the study of LIS because of its wide wavelength tunability. However there are several disadvantages in comparison with TEA-CO_2 laser. A TEA-CO_2 l[illegible] used to provide light pulses of the peak power of a few megawatts with the pulse duration of one hundred nanoseconds and with a very narrow spectral bandwidth, the bandwidth being less than 0.1 cm^{-1}. The power per one pulse can be a few joules. On the other hand, the temporal structure of the light from MIR-FEL of the IR FEL Research Center, which is used in this study, is composed of a series of macro pulses with the duration of 2 micro-seconds and the repetition rate of less than 10 pps, and each of these macro pulses is consisting of micro pulses with the duration of 2 pico-seconds and with the interval of 350 pico-seconds[1]. Although the peak power of a micro pulse is as large as a few megawatts, the power per one micro pulse is only [illegible] 8-2 μ J and the power per one macro pulse is about 150 mJ. The spectral bandwidth is significantly larger than that of TEA-CO_2 laser, it being about 0.5 % of the wavelength.

The energy of a micro pulse of MIR-FEL may be too small to induce an infrared multi-photon dissociation (IR MPD) of a target molecule unless the light beam is strongly focused into an extremely small area. On the other hand, a macro pulse of the FEL seems be intense enough to excite the molecule up to high vibrational levels by the multi-photon process, from which the multi-photon dissociation could be induced by the subsequent irradiation with a strong pulse of TEA-CO_2 laser as illustrated in Fig. 1. It is well known that vibrational pre-excitation greatly enhances the IR MPD of a polyatomic molecule [2,3]. Therefore, such two-lasers scheme may be more effective for LIS of a silicon-containing molecule in comparison with the case of using a single laser.

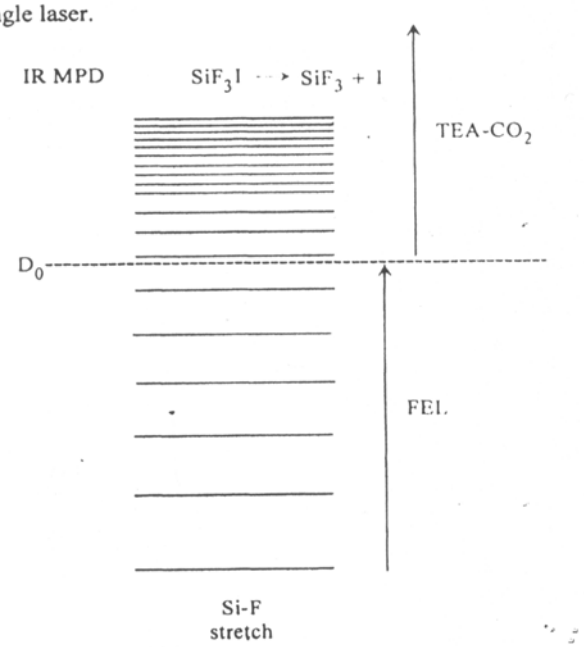

Fig. 1. Schematic energy level diagram for IR MPD of vibrationally pre-excited SiF_3I.

It has been already demonstrated that the enrichment of a particular Si isotope could be performed by using a MDP reaction induced with a strong infrared laser [3-8]. But, all of those works were carried out by using Si_2F_6 as the working material except the two cases, which used SiF_4 [6] or SiH_4 [3].

In this paper we report, for the first time, the results of the experimental study on the multi-photon dissociation of SiF_3I.

2. Experimental Apparatus

We have constructed an apparatus for the investigation of isotope separation by use of FEL. The apparatus has been installed at the beam port in Laboratory 2 of the IR FEL Research Center. Figure 2 shows the schematics of the constructed apparatus, the details of which will be reported elsewhere in this proceedings. The reaction chamber is made of a cylindrical stainless steel tube with the internal diameter of 4 cm and the length of 50 cm, ZnSe windows being installed at the both ends of the chamber. The sample gas flows into the reaction chamber through two inlets near the windows and flows out through the outlet at the center of the chamber. This configuration makes a gas flow from the windows to the center of the chamber and helps to avoid the contamination of the windows by the reaction products, which may result in a decrease of the light transmission of the windows. The reaction chamber is connected to the circulation loop equipped with a ventilation fan. The gas flow rate in this circulation loop was estimated to be about 30 *torr l / sec*. The gas flows out from the reaction chamber and reenters into the chamber after passing through a cold trap, which is supposed to trap specified reaction products. The analysis of the reaction products and the measurement of the isotope content are made by use of the FT/IR spectrometer and the Q-mass spectrometer installed in the circulation loop.

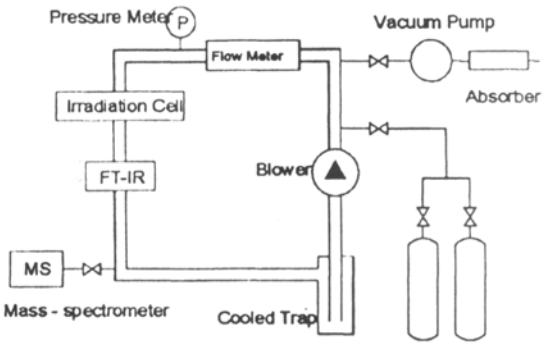

Fig. 2. Schematics of the experimental arrangement.

Selection of working substances

A working substance for the laser isotope separation is required to have a large isotope shift of infrared absorption band together with low dissociation energy in order to achieve a high isotopic enrichment factor and a high efficiency. Based on this idea, we paid attention to the silicon-containing molecules where the atoms other than silicon are isotope-free. Among halogens, fluorine (^{19}F) and iodine (^{127}I) are known to be isotope-free. The simple halide molecules that are formed by the combination of these halogens are SiF_4, SiF_3I, SiF_2I_2, $SiFI_3$, and SiI_4. We carried out the screening of working material by means of quantum chemical calculations. Among the four compounds mentioned above, SiF_3I [9] was found to be the most promising material for MPD experiment, since it has the smallest dissociation energy. The methods and the results of this quantum chemical calculations will be described later.

The SiF_3I sample used in the present experiments was synthesized and purified at the Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia. The only detectable impurity in the sample was ~ 0.5% SiF_4, as determined from the infrared spectrum of SiF_3I.

MPD experiments by TEA-CO_2 laser

The temporal structure of the light from the TEA-CO_2 laser used in this study has an initial spike of 100 ns (FWHM) and 2 μs tail. The properties of the light from this TEA-CO_2 laser are as follow: wavelength is 10.6 μm, pulse energy is 1 J, pulse duration is 200 ns, and repetition rate is 10 Hz. The laser beam with a square spatial profile of 2cm × 3cm, was focused by a ZnSe lens having the focal length of 30 cm, the lese being installed at 5cm from the ZnSe window. The initial pressure of the SiF_3I gas filled in the reaction chamber was 5 torr.

MPD experiments by the co-irradiation with FEL and TEA-CO_2 laser

The method of experiment is almost the same as the one mentioned above, except that the co-irradiation was made by the light from MIR-FEL. Fixing the wavelength of TEA-CO_2 laser at 10.6 μm, we investigated the effect of the wavelength of FEL light over the 10 μm spectral region. FEL beam was focused by Zn-Se lens with the focal length of 1300 cm to make the diameter of the irradiated region in the reaction chamber to be about 2 mm. The initial pressure of the SiF_3I in the reaction chamber was 5 torr also in this experiment.

3. Results and discussions

On-line analysis of the working mixture was carried out by FT/IR spectroscopy. The IR spectrum of the working gas in the spectral region from 650 cm^{-1} to 5000 cm^{-1} was measured at every 2 minutes during the irradiation. The spectral change caused by the co-irradiation with the 955 cm^{-1}

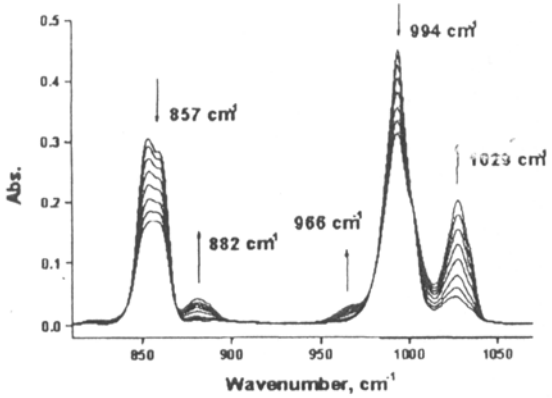

Fig. 3 Change of the IR spectrum of SF_3I during the co-irradiation by FEL at 955 cm^{-1} and TEA-CO_2 laser at 946 cm^{-1}; IR spectrum was measured every 2 minutes.

light of FEL and the 946 cm^{-1} light of TEA-CO_2 laser is shown in Fig. 3. The intensities of the 857 cm^{-1} and 994 cm^{-1} bands of SiF_3I decreased with irradiation time and new absorption bands appeared at 882 cm^{-1}, 966 cm^{-1} and 1029 cm^{-1}. A

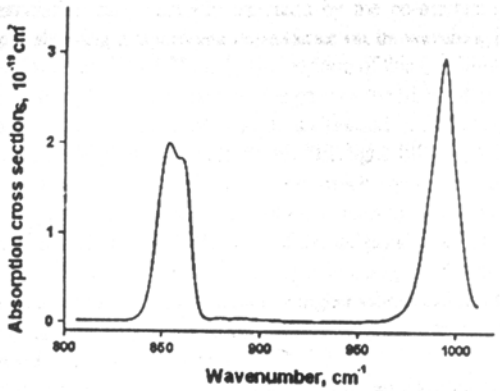

Fig. 4. Infrared spectrum of SF_3I.

Table 1. IR spectrums (cm^{-1}) of SiF_4, SiF_3I and SiF_2I_2

SiF_4, ref. [9]	SiF_3I, ref. [10]	SiF_2I_2, ref. [10]
1025	323	225
800	339	384
389	407	453
268	473	494
	477	883
	481	890
	491	968
	494	
	853	
	858	
	864	
	995	

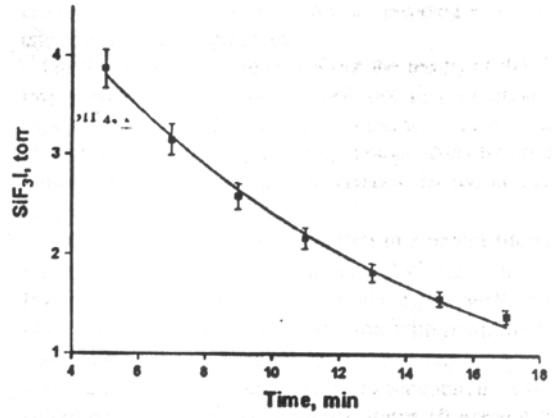

Fig. 5 Change of the concentration of SF_3I with time during the co-irradiation by FEL at 975 cm^{-1} and TEA-CO_2 laser at 946 cm^{-1}; dots are experimental data and solid line is approximation using Equation (4).

similar spectral change was observed also in the case of the irradiation with the 946 cm^{-1} light of TEA-CO_2 laser only. We can consider that the main products formed by the reactions accompanying the MPD of SF_3I are iodofluorosilanes. Thus we compared the observed data with the reported IR spectra of iodofluorosilane molecules (Table 1) [9,10] and found that the new bands were assignable to SiF_4 (1029 cm^{-1}) and SiF_2I_2 (882 cm^{-1} and 966 cm^{-1}).

Thus, we can conclude that the main side-reactions following the multi-photon dissociation of SiF_3I are the formations of SiF_4 and SiF_2I_2. The reactions taking place in the reaction chamber could be described as follows:

a) multi-photon dissociation of SiF_3I

$$SiF_3I + nh\nu \longrightarrow SiF_3 + I \qquad (1)$$

b) formation of SiF_4

$$SiF_3 + SiF_3I \longrightarrow SiF_4 + SiF_2I \qquad (2)$$

c) formation of SiF_2I_2

$$SiF_2I + SiF_3I \longrightarrow SiF_2I_2 + SiF_3 \qquad (3)$$

We estimated the concentration of SiF_3I from the observed intensity of the peak at 857 cm^{-1}.shown in Fig. 4. Figure 5 shows an example of the observation on the change of the SF_3I concentration with time during the co-irradiation with FEL and TEA-CO_2 laser. Since the multi-photon dissociation of SF_3I is an unimolecular process, the time dependence of the concentration of SiF_3I can be expressed by the following equation:

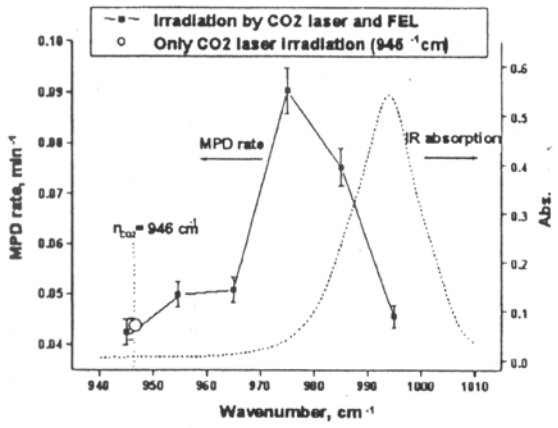

Fig. 6. Infrared spectrum (dashed line, right axis) and reaction spectrum (left axis) for 5 torr of SF_3I irradiated by both FEL and TEA-CO_2 laser (squares) and by single TEA-CO_2 laser (circle) in the region of the 10 μm absorption band.

$$[SiF_3I] = [SiF_3I]_0 \exp(-kt) \qquad (4),$$

where k is the rate constant. Assuming Equation (4), we estimated the value of the rate constant k for the multi-photon dissociation of SF_3I by the co-irradiation of FEL and the 946 cm^{-1} light of TEA-CO_2 laser, from the data like Fig. 5 obtained for different wavelengths of the co-irradiating FEL light.

International Symposium on IR-FEL and its ApplicationThe results are shown with solid squares in Fig. 6, where the dissociation rate obtained for the irradiation with the 946 cm^{-1} light of TEA-CO_2 laser only, is shown with a open circle at the wavelength of 946 cm^{-1}. The broken line in Fig.6 is the infrared spectrum of SF_3I. We can clearly see in this figure that the dissociation rate markedly increases by the co-irradiation of FEL light, showing a significant dependence on its wavelength with the maximum at about 975 cm^{-1}. The position of this maximum is lower by ~ 16 cm^{-1} as compared with the peak of the IR band of SiF_3. The above experimental results can be understood in the following way. By the multi-photon excitation with FEL light, SiF_3I molecule is first excited to a pre-excited state, from which the dissociation by the multi-photon excitation by the 946 cm^{-1} light of TEA-CO_2 laser can be effectively induced. Because of the unharmonicity of vibrational levels, the wavenumber of FEL light working for the multi-photon excitation to the pre-excited state (a higher vibrational level) becomes to be significantly lower in comparison with the wavenumber of the lowest vibrational excitation.

All the data obtained in the present study clearly indicate that the muli-photon dissociation of SF_3I can be effectively induced by the co-irradiation with FEL and TEA-CO_2 laser. Since the bandwidths of the irradiating lights are smaller than the isotope shift of the concerned IR band of SF_3I, there is a good reason for us to expect the appearance of isotope selectivity in the multi-photon dissociation process. However, no indication for isotope selectivity was detectable in the present study. This fact indicates that some rapid isotope exchange reactions are taking place in the working mixture under the irradiation. The followings would be the most possible candidates of the isotope exchange reaction:

$$^{\bullet}SiF_3 + SiF_3I \longrightarrow {}^{\bullet}SiF_3I + SiF_3 \qquad (5)$$

and

$$^{\bullet}SiF_2I + SiF_3I \longrightarrow {}^{\bullet}SiF_3I + SiF_2I \qquad (6)$$

Thus we concluded that, in order to achieve isotope separation by use of the multi-photon dissociation of SF_3I, we have to add some material, scavenger, that reacts very rapidly with the free radical SiF_3 to form stable chemical species and avoid the isotope exchange reactions like (5) and (6). NOCl, O_2 and/or NO_x might be the candidates of such scavenger. We are planning to investigate the effect of those scavenger gases.

Finally, we wish to mention about the results of the theoretical investigations that we have carried out in connection with the experimental studies described here. First, we estimated the infrared absorption bands of SiF_3I and their isotope shifts by *ab initio* and semi-empirical molecular orbital methods, by use of the Gamess program package[11].

According to the results reported in a recent literature, the vibrational frequencies computed by the semi-empirical PM3, AM1, and MNDO methods agree well the values obtained by the *ab initio* calculation with medium size basis sets. Among these three methods, PM3 has been reported to give closest agreement with experimental values, the calculated values being generally about 10 percent higher in comparison with the experimental values for the frequencies of stretching vibrations[12]. We carried out calculations of molecular geometry and harmonic vibrational frequencies on SiF_3I molecule by the semi-empirical RHF PM3 method [16] and by the *ab-initio* UHF method with the 6-311G basis set [13-15]. In Table 2, the calculated structure parameters of SiF_3I are compared with the corresponding experimental data [17]. The calculated frequencies in the 10 μm and 12 μm spectral regions are presented in Table 3. The isotope shift was found to be largest for Si-F stretching mode (in the 10 μm spectral region). The results given in Table 3, show that the isotope shift of this vibrational mode is 18.2 cm^{-1} between $^{28}SiF_3I$ and $^{29}SiF_3I$, and 8.6 cm^{-1} between $^{29}SiF_3I$ and $^{30}SiF_3I$ in the case of UHF 6-311G *ab-initio* calculations. The RHF PM3 semi-empirical method gives also similar results: 8.6 cm^{-1} between $^{28}SiF_3I$ and $^{29}SiF_3I$, and 8.1 cm^{-1} between $^{29}SiF_3I$ and $^{30}SiF_3I$.

Table 2. Structural parameters of SiF_3 molecule

	calculated		obseved (Ref. [15])
	UHF 6-311G	RHF PM3	
Si-F (A)	1.62	1.56	1.563(4)
Si-I (A)	2.45	2.52	2.381(3)
F-Si-F (°)	107.23	112.26	108.24(13)
F...F (A)	2.61	2.60	2.532(7)

Table 3. Harmonic frequencies (cm^{-1}) of $^{28}SiF_3I$, $^{29}SiF_3I$, $^{30}SiF_3I$ in the 10 μm spectral region

	UHF6-311G	RHF PM3	Ref. [10]
^{28}SiF3I	977.5	988.3	995
^{28}SiF3I	969.3	979.7	-
^{30}SiF3I	961.6	971.6	-

Table 4. Calculated IR spectrum (cm^{-1}) of the vibrationally excited $^{28}SiF_3I$ molecule at different levels of the excitation in the 10 μm spectral region

Vibrational level of $^{28}SiF_3I$	Multimode with RHF PM3
0	986.3
1	984.1
2	981.9
3	979.7
4	977.5
5	975.3
6	973.1
7	970.9
8	968.8
9	966.7

Since RHF PM3 semi-empirical method is rather fast and gives good accuracy for the predicted structure parameters of SiF_3I (see Table 2) and harmonic frequencies for Si-F stretching mode (see Table 3), it is interesting to apply this semi-empirical method for the prediction of unharmonic frequencies of the vibrationally excited states of SiF3I. The calculations were carried out by using the software package, which we developed by uniting the Multimode[18] and the Gamess program packages. The calculations were made on the bases of the vibrational self-consistent field (VSCF) method, without mode coupling, and for angular momentum J = 0. Predicted IR bands of the vibrationally excited states of $^{28}SiF_3I$ molecule are presented in Table 4. The results given in Table 4 indicate that in order to give a red shift of

~ 16 cm^{-1}, SiF_3I molecule should be excited to the 7th vibrational level. This number approximately coincides with the experimentally estimated number of the photons of FEL light contributing to produce the pre-excited state contributing to the MPD process of SiF_3I.

4. Conclusions

We studied the MPD of SiF_3I by use of FEL and TEA-CO_2 laser and found that the MPD of SiF_3I could be effectively induced by the co-irradiation with the 946 cm^{-1} light of TEA-CO_2 and FEL light in the 10 μm region and that enhancement of MPD rate constant markedly depends on the wavelength of FEL light. The maximum in the plots of MPD rate against the wavelength of the co-irradiating FEL light was found to be located at the position red-shifted by about 16 cm^{-1} from the peak position of the corresponding IR band. Although we could get evidence for that the MPD of SiF_3I can be induced by the co-irradiation with FEL and TEA-CO_2 laser and the main final product of this process are SiF_4 and SiF_2I_2, we could not detect any indication of isotope selectivity in the above process. This was considered to be due to the presence of rapid side-reactions, which result in a fast isotope exchange. Thus it was concluded that the use of a suitable scavenger material is indispensable for realizing isotope separation by use of the MPD of SiF_3I.

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