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Silicon isotope-selective multiphoton dissociation of 1,2-dichloroethyltrifluorosilane

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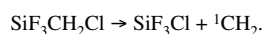
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The IR laser induced unimolecular decomposition of SiF₃CHClCH₂Cl reveals a high efficiency and a high silicon isotope selectivity.

The multiple photon decomposition (MPD) of molecules induced by strong pulsed IR laser radiation is a promising method for laser based isotope separation technology.^{1,2} Haszeldine with co-authors^{3,4} studied the thermal decomposition of halogen-substituted alkylsilicon compounds, in which a halogen is present at the α - or β -carbon relative to silicon and found that these compounds underwent unimolecular decomposition involving halogen transfer from carbon to silicon. Recently,⁵ we suggested that such reactions are promising for selective processes induced by IR laser radiation due to their relatively low dissociation thresholds. In particular, we studied the IR MPD of SiF₃CH₂Cl under exposure to CO₂-laser radiation. The insertion of a chlorine atom onto α -carbon significantly improves the characteristics of the silicon isotope-selective dissociation as compared with a similar molecule of SiF₃Me without the chlorine atom on carbon.⁶ The disadvantage of SiF₃CH₂Cl from the point of view of the selective IR MPD is that one of the products of its decomposition is singlet methylene:



The singlet methylene ¹CH₂ is a very reactive intermediate,⁷ which initiates a complex sequence of secondary reactions. Therefore, the halogen-substituted alkylsilicon compounds with a halogen atom on the β -carbon are more appropriate for selective IR MPD since stable products are formed in the unimolecular decomposition of such molecules: halogenated silane and olefin molecules.

The best results on the silicon isotope-selective IR MPD of Si-containing molecules were obtained^{8–10} in the experiments with the Si₂F₆ molecule. However, the Si₂F₆ molecule has an evident disadvantage for silicon isotope-selective processes because it contains two silicon atoms. The minor isotopes are contained mostly in isotopically mixed molecules such as F₃²⁸Si–²⁹SiF₃ and F₃²⁸Si–³⁰SiF₃. This fact limits the isotopic effect since during the dissociation of such isotopically mixed molecules the ²⁸Si isotope and the minor one (²⁹Si or ³⁰Si) would pass into products equally. Previously,^{6,11} we assumed that a higher isotope selectivity can be achieved for a molecule with only one silicon atom.

Here, we report an experimental study of the IR multiphoton dissociation of SiF₃CHClCH₂Cl under the action of a CO₂ laser. Essentially high silicon isotope selectivities were achieved in these experiments. The experiments demonstrate the advantage of using halogen-substituted alkylsilicon compounds, in which

a halogen is present on β -carbon relative to silicon, as the objects of silicon isotope-selective IR MPD.

SiF₃CHClCH₂Cl was synthesised from SiCl₃CHCH₂. At the first stage SiCl₃CHCH₂ was converted to SiF₃CHCH₂ using the reaction with SbF₃. Then, equal amounts of gaseous SiF₃CHCH₂ and Cl₂ were mixed in a glass vessel. After that, the mixture was exposed to weak UV light through quartz windows. The SiF₃CHClCH₂Cl formed was separated from the reaction mixture by fraction condensation.

The samples of neat SiF₃CHClCH₂Cl with the natural abundance of silicon isotopes were irradiated. The reaction cell was a 200 cm³ Pyrex-glass cylinder 2 cm in diameter with NaCl windows. The cell was connected to the ion source of a mass spectrometer through a glass pinhole about 20 μ m in diameter. Therefore, the cell contents could be analysed at any moment during laser irradiation. As a source of IR radiation, a homemade tunable pulse TEA CO₂ laser was used. The maximum pulse energy of the laser was about 5 J. The laser pulse had a fwhm of about 100 ns, with a nitrogen tail of about 1.5 μ s duration and containing about 50% of the laser pulse energy. The laser beam was collimated in front of the input window of the cell by an iris 1 cm in diameter.

Using quantum chemical calculations [B3LYP, 6-31G(p,d) basis set] we found that the energetically lowest pathway for the unimolecular decomposition of SiF₃CHClCH₂Cl was the channel with chlorine atom transfer from β -carbon to silicon:



The activation threshold for this channel was found about 184 kJ mol⁻¹. For comparison, the activation barrier of Si₂F₆ decomposition is about 188 kJ mol⁻¹.⁹

For the other channel of the unimolecular decomposition of SiF₃CHClCH₂Cl with chlorine atom transfer from α -carbon to silicon



the reaction threshold was found > 280 kJ mol⁻¹.

The IR spectrum of SiF₃CHClCH₂Cl has a strong peak with a maximum at 991 cm⁻¹. It corresponds to the absorption band of Si–F stretching vibrations. The significant dissociation of SiF₃CHClCH₂Cl was observed, when the reaction cell containing the sample molecules was irradiated with the CO₂ laser tuned to the 10 R(38) laser line 986.57 cm⁻¹, which is close to the peak maximum. In some experiments, more than 50% of sample

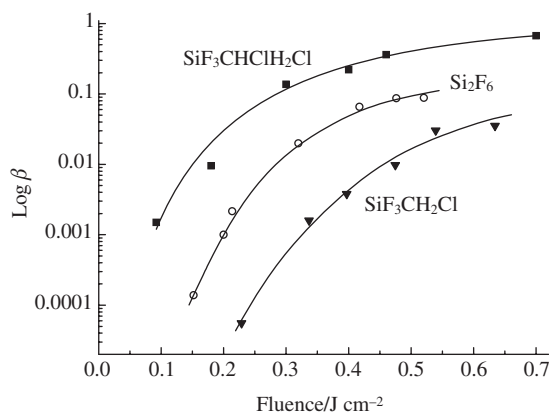


Figure 1 The laser fluence dependence of the IR MPD probability β for different sample molecules: solid squares – $\text{SiF}_3\text{CHClCH}_2\text{Cl}$ (this work), open circles – Si_2F_6 ,¹⁰ solid triangles – $\text{SiF}_3\text{CH}_2\text{Cl}$.⁵

molecules in the irradiated volume were decomposed as a result of just a single laser pulse.

The mass-spectrometric analysis of the reaction cell contents after the irradiation showed that the decomposition products were SiF_3Cl and CHCH_2Cl in an equal ratio, and the amount of each product formed, either SiF_3Cl or CHCH_2Cl , was equal to the amount of the $\text{SiF}_3\text{CHClCH}_2\text{Cl}$ consumed in the reaction. No other products were found. From this analysis, we can conclude that the multiphoton dissociation under our experimental conditions follows the lowest dissociation channel (1).

Figure 1 presents the laser fluence dependence of the IR MPD probability β (the averaged probability of a single molecule to dissociate during a single laser pulse) for $\text{SiF}_3\text{CHClCH}_2\text{Cl}$ molecules. The laser was tuned to 986.57 cm^{-1} . For comparison, data^{5,10} for Si_2F_6 and $\text{SiF}_3\text{CH}_2\text{Cl}$ are shown. The efficiency of $\text{SiF}_3\text{CHClCH}_2\text{Cl}$ dissociation is high: at the same energy fluence, the probability of dissociation of $\text{SiF}_3\text{CHClCH}_2\text{Cl}$ is higher than that of Si_2F_6 by a factor of 3–5 or $\text{SiF}_3\text{CH}_2\text{Cl}$ by a factor of 10.

When the sample molecules were irradiated with CO_2 laser radiation tuned into the 10R branch ($\nu > 975\text{ cm}^{-1}$), the silicon isotopic composition of the SiF_3Cl product was almost the same as the natural one. If the laser was tuned to the 10P branch ($\nu < 955\text{ cm}^{-1}$), we observed the preferred dissociation of the molecules with the rare silicon isotopes ^{29}Si and ^{30}Si . Figure 2 shows the time dependence of the intensities of two mass-spectral lines of the SiF_3Cl mass spectrum during laser irradiation. The lines with m/z 120 belong to the $^{28}\text{SiF}_3^{35}\text{Cl}^+$ ion, and the line with m/z 122 belongs to the $^{30}\text{SiF}_3^{35}\text{Cl}^+$ and $^{28}\text{SiF}_3^{37}\text{Cl}^+$ ions. The growth rate of the line with m/z 122 line is roughly five times higher than that of the line with m/z 120. Taking into account the natural abundances of silicon isotopes in the

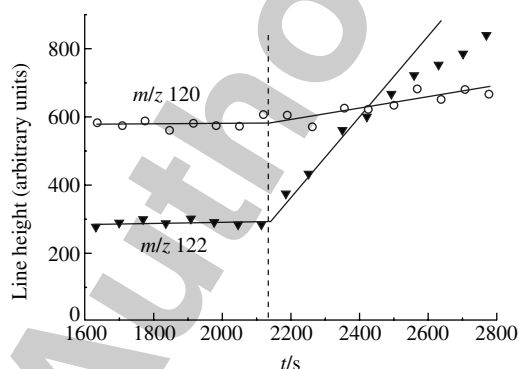


Figure 2 Evolution of SiF_3Cl^+ mass-spectrometric line intensities during the irradiation of $\text{SiF}_3\text{CHClCH}_2\text{Cl}$. The laser radiation wavenumber was 956 cm^{-1} . The vertical dashed line indicates the moment when the laser was switched on.

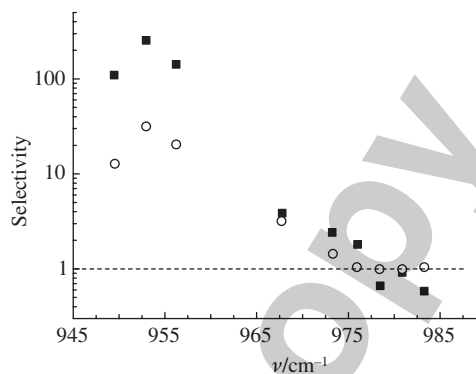


Figure 3 The laser-radiation wavenumber dependence of the isotopic selectivity S_{30} (solid squares) and S_{29} (open circles) of the IR MPD of $\text{SiF}_3\text{CHClCH}_2\text{Cl}$. The sample pressure was 40 Pa (0.3 Torr); the laser radiation fluence was 0.3 J cm^{-2} . The approximate laser pulse duration was about 100 nm at fwhm with the nitrogen tail of about 1.5 μs .

reagent, namely, 92.27% for ^{28}Si and 3.05% for ^{30}Si , we can estimate the relative rate of dissociation of ^{30}Si -containing molecules to be about 150 times higher than the relative rate of ^{28}Si -containing molecules.

The intensities of lines in Figure 2 before the laser was switched on are nonzero because of the contribution of the mass spectra of $\text{SiF}_3\text{CHClCH}_2\text{Cl}$. This contribution complicates the quantitative analysis of the isotopic contents of SiF_3Cl . To be sure that the observed high isotopic selectivity is not an artifact caused by the overlapping of the mass spectra of different components of a complex gaseous mixture, we separated SiF_3Cl after irradiation by fractional condensation. Taking into consideration the chlorine isotopes ^{35}Cl and ^{37}Cl during the isotopic analysis of the extracted SiF_3Cl , based on lines with m/z 120–124, we obtained for the Si isotopic composition of SiF_3Cl after the irradiation: 14.9% ^{28}Si , 15.5% ^{29}Si and 69.6% ^{30}Si .

Comparing these numbers with the natural isotopic composition 92.27% ^{28}Si , 4.68% ^{29}Si and 3.05% ^{30}Si , we obtain the isotopic selectivities (ratio of the IR MPD probabilities of the sample molecules containing different silicon isotopes): $S_{30} = \beta_{30}/\beta_{28} = 141$; $S_{29} = \beta_{29}/\beta_{28} = 20$.

Figure 3 presents the radiation wavenumber dependence of the isotopic selectivities S_{30} and S_{29} . This dependence was obtained by tuning the CO_2 laser radiation to different rotational laser lines. The region $957\text{--}967\text{ cm}^{-1}$ corresponds to the gap between 10P and 10R branches. All the experimental points in Figure 3 were obtained at a $\text{SiF}_3\text{CHClCH}_2\text{Cl}$ pressure of 40 Pa (0.3 Torr). At $\nu = 952.9\text{ cm}^{-1}$, we made the measurements at higher pressures. The selectivities remained the same up to at least 133 Pa (1 Torr). Note that the total laser pulse duration was about 1.5 μs including the nitrogen tail.

Thus, the study of the IR multiphoton dissociation of $\text{SiF}_3\text{CHClCH}_2\text{Cl}$ confirms the previously made suggestion that the laser induced unimolecular decomposition of halogen-substituted alkylsilicon compounds, in which a halogen is present on β -carbon relative to silicon, should possess both a high efficiency and a high selectivity of the process. The parameters obtained in our experiments on the silicon isotope-selective IR multiphoton dissociation of $\text{SiF}_3\text{CHClCH}_2\text{Cl}$ are higher than those for other silicon-containing molecules.

The maximum selectivity for ^{30}Si was reached as high as 240 in our experiments, significantly higher than that for Si_2F_6 , the molecule for which the IR multiphoton dissociation was considered as a base for the laser technology of silicon isotope separation.^{8,9}

Let us also emphasize the fact that, the selectivity for ^{29}Si , achieved in our experiments, was essentially high. In all previous studies ^{29}Si could not be enriched at any significant level.^{5,6,8–12}

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