

IR multiphoton dissociation of trichlorosilane induced by pulsed CO₂ and NH₃ laser radiation

V.M. Apatin, V.B. Laptev, E.A. Ryabov

Abstract. The IR multiphoton dissociation of trichlorosilane (SiHCl₃) molecules irradiated by pulses from CO₂ and NH₃ lasers is studied. The dependences of the dissociation yield on the frequency and energy density of laser radiation, as well as on the parent pressure of SiHCl₃, are determined. It is found that HCl and a solid precipitate, probably with a common chemical formula (SiCl₂)_n, are the main products of dissociation of trichlorosilane.

Keywords: IR multiphoton dissociation, trichlorosilane, selectivity.

1. Introduction

The interest of researchers has been growing in recent years towards the investigations of isotopically pure silicon [1–5], a prospective material for microelectronics, especially in view of its higher thermal conductivity as compared to silicon of natural isotopic composition [1]. (The natural abundance of silicon isotopes is ²⁸Si – 92.23 %, ²⁹Si – 4.67 %, ³⁰Si – 3.10 %.) This requires optimisation of conventional methods and the development of new competitive methods of isotope separation.

At present, one of the most developed methods of laser separation of light and medium isotopes (see Ref. [6] and Sections 7.3 and 7.4 in Ref. [7]) is the method of isotopically selective IR multiphoton dissociation (MPD) of molecules. Many experiments were carried out in order to ascertain the possibility of using this method for separating silicon isotopes. For this purpose, pulsed CO₂ laser radiation tuned in resonance with the molecular vibrations of the corresponding isotopic component of the Si – F bond in SiF₄ [8], Si₂F₆ [9–13], SiF₃CCl₃ and (SiF₃)₂O [14], SiF₃CH₃ and SiF₃C₆H₅ [15] was used. However, in spite of the high yield and/or selectivity of dissociation attained in these processes, further progress in this direction was halted due to the fact that these compounds are not produced on mass scale and therefore cannot be used as a substance for large-scale laser separation of isotopes (LSI).

The silicon containing compounds widely used in industrial microelectronics and silico-organic synthesis are

silane and its chlorine substitutes (mainly tri- and dichlorosilanes SiHCl₃ и SiH₂Cl₂) and siloxanes. Selective MPD of the molecules of two siloxanes (Si(OCH₃)₄ and [(CH₃)₃Si]₂O) under the action of pulsed CO₂ laser radiation on the Si–O–Si(C) vibrational bonds was studied in Ref. [16]. No experiments have been conducted to study the LSI of silicon using tri- and dichlorosilane, in spite of the fact that isotopically selective excitation of these molecules is possible using the IRLAPS method (IR laser assisted photofragment spectroscopy) [17, 18], which is analogous to the two-frequency IR MPD method (see Section 6.4 in Ref. [6]).

When applied to the separation of silicon isotopes, the essence of this method lies in a preliminary selective excitation of the required molecular isotopic component to the vibrational quasicontinuum up to a level ~ 4300 cm⁻¹ due to a single-quantum IR absorption at the first overtone of the high-frequency vibration of the Si – H bond. After this it continues to get excited in the quasicontinuum right up to dissociation limit due to multiphoton absorption of the CO₂ or NH₃ laser radiation that is resonant to the corresponding low-frequency vibration, but only for molecules in the quasicontinuum. Laboratory experiments on isotopically selective dissociation of silane showed [18] that this method allows a very high enrichment (more than 96 %–99 %) for all isotopes of silicon.

In this paper, we present the first results of IR multiphoton dissociation of SiHCl₃ molecules under the action of pulsed CO₂ or NH₃ laser radiation. The dependences of dissociation yield on the frequency and energy density of laser radiation, as well as on the parent pressure of SiHCl₃, are obtained.

2. Experiment

2.1 Dissociation of SiHCl₃ by CO₂ laser radiation

Experiments on excitation and dissociation of trichlorosilane by pulsed CO₂ laser radiation were carried out by exciting the mixed band of the 2ν₂ overtone and the composite (ν₄ + ν₆) vibration, at the frequency 984 cm⁻¹ [19]. Radiation of frequency 975.9 cm⁻¹ (10R20 line) and energy 0.6–0.9 J passed through a lens of focal length 20 cm and was directed into a cell of length 10 cm containing SiHCl₃ under a pressure of 1–3 Torr. The energy density in the waist in the middle of the cell was 50–80 J cm⁻².

When radiation was tightly focused, the laser beam cross section and related energy density and MPD yield varied strongly along the length of the cell. Hence, for simplicity,

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Received 16 September 2002; revision received 5 March 2003

Kvantovaya Elektronika 33 (10) 894–896 (2003)

Translated by Ram Wadhwa

we used as a quantitative characteristic of dissociation the dissociation yield β averaged over the volume and defined as the fraction of molecules dissociated during one laser pulse over the entire volume by neglecting the change in the yield in this volume. The yield was calculated from the decrease in the intensity of the IR absorption band of trichlorosilane recorded with a SPECORD-M82 automated IR spectrophotometer before and after irradiation. The dissociation products were also detected and identified from the IR spectra.

As the radiation energy increased from 0.6 to 0.9 J, the average dissociation yield increased from 0.14 % to 0.35 % at a SiHCl_3 pressure of 2 Torr. A decrease in the SiHCl_3 pressure down to 1 Torr causes a decrease in β by a factor of 1.5. We failed to detect any dissociation products, probably due to small quantities of the dissociated trichlorosilane and a limited sensitivity of the method used for analysis. Optical breakdowns of the gas were observed sometimes upon an increase in the SiHCl_3 pressure to 3 Torr, and the consumption of trichlorosilane increased abruptly. After this, only one gaseous product (HCl) was detected, and a precipitate having a single IR absorption band with centre at $\sim 590 \text{ cm}^{-1}$ was observed on the cell windows. Because the vibration of the Si – Cl bond falls in this frequency range, we presume in analogy with thermal [20–22] and laser [23] pyrolysis of trichlorosilane that the precipitate deposited on the windows of the cell was a polymer of the type $(\text{SiCl}_2)_n$.

Thus, our experiments showed that the dissociation of SiHCl_3 by pulsed CO_2 laser radiation action on the $2\nu_2$ overtone and composite ($\nu_4 + \nu_6$) vibration is possible, but requires a very high radiation energy density (50–80 J cm^{-2}). For this reason, we switched over to experiments on the excitation and dissociation of trichlorosilane by NH_3 laser radiation tuned in resonance with the deformation vibration of the Si – H bond.

2.2 Dissociation of SiHCl_3 by NH_3 laser radiation

The deformation vibration of the Si – H bond at the frequency $\nu_4 = 810.8 \text{ cm}^{-1}$ was used to excite trichlorosilane by NH_3 laser radiation [19].

We used an NH_3 laser, which was pumped by the pulsed CO_2 laser radiation. In the NH_3 laser tuning range 770–890 cm^{-1} , the maximum output energy $\sim 140 \text{ mJ}$ was obtained at frequencies 853, 828 and 816 cm^{-1} . The radiation pulse had a duration of 1 μs and consisted of a leading peak with a FWHM of 200 ns followed by a ‘tail’ containing 50 %–70 % of the total energy. The radiation was focused to a gas-filled cell by a lens of focal length 10 cm. In order to prevent a strong absorption of the laser radiation passing through the cell with a high pressure of trichlorosilane, cells of different lengths (2, 3 or 6.6 cm) were used. The cross-sectional area of the beam in the waist was $\sim 1 \text{ mm}^2$. The radiation energy was usually equal to 25–60 mJ. The dissociation yield β averaged over the irradiated volume, which was defined above, was also used as a quantitative parameter of MPD.

At first, the dependence of the dissociation yield of the $^{28}\text{SiHCl}_3$ molecules on the laser frequency $\Omega_{\text{las}} = 816, 809.7, 797, 789$ and 780 cm^{-1} was determined (Fig. 1). The maximum of the multiphoton dissociation spectrum is noticeably shifted to the red relative to the linear IR absorption band ν_4 , which is typical of MPD molecules [6]. The maximum yield was achieved at the NH_3 laser

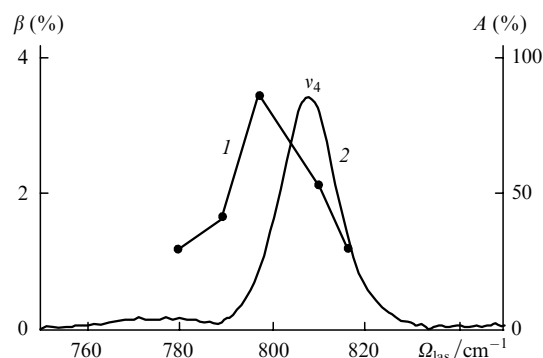


Figure 1. Dependence of the dissociation yield β of $^{28}\text{SiHCl}_3$ molecules on laser radiation frequency Ω_{las} (curve 1) and the linear IR absorption band A of trichlorosilane (curve 2) for $E_{\text{las}} = 40 \text{ mJ}$ and an SiHCl_3 pressure of 8 Torr.

frequency $\Omega_{\text{las}} = 797 \text{ cm}^{-1}$ at which all subsequent experiments were carried out.

The dependences of the dissociation yield on the energy E_{las} (or the energy density) of laser radiation was measured at $\Omega_{\text{las}} = 797 \text{ cm}^{-1}$ and under the parent pressure of SiHCl_3 equal to 0.5, 1 and 3 Torr (Fig. 2). For all values of the pressure used in the measurements, the dependences had the form $\beta \sim E^{1.5}$, which is typical of focused geometry of radiation [24, 25]. The dependence $\beta(E_{\text{las}})$ obtained under a pressure of 0.5 Torr, i.e., under conditions close to collision-free regime, allows us to estimate the MPD threshold for trichlorosilane at about 3 J cm^{-2} .

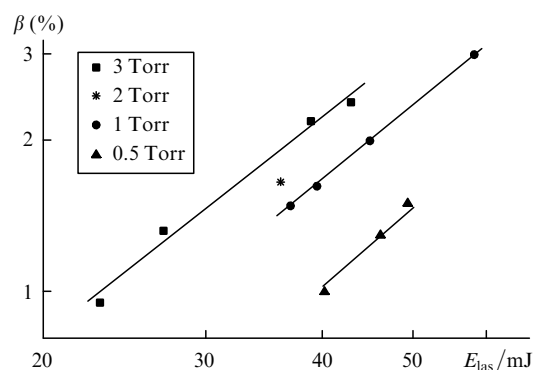


Figure 2. Dependences of the dissociation yield β of SiHCl_3 molecules on laser radiation energy E_{las} for various values of the SiHCl_3 pressure.

Figure 3 shows the dependence of the SiHCl_3 dissociation yield on its parent pressure. For $E_{\text{las}} = 35 \text{ mJ}$ and a pressure exceeding 1 Torr, β is found to increase almost linearly with pressure. At pressures below 1 Torr, the dissociation yield tends to a constant value of 0.6 %–0.7 %, which apparently points towards the approaching collision-free regime of IR multiphoton excitation.

After MPD of SiHCl_3 , the only gaseous product detected was HCl. Within the measurement error, the quantity of HCl was found to conform to the amount of dissociated trichlorosilane. After a series of experiments, the IR spectra revealed the presence of a precipitate deposited on the cell windows and having a quite broad (FWHM $\sim 50 \text{ cm}^{-1}$) absorption band centred at $\sim 600 \text{ cm}^{-1}$. Because the vibration of the Si – Cl bond falls in this range, we associate this band with the deposition of a

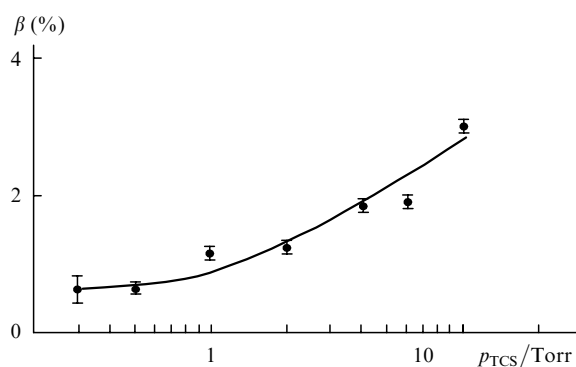


Figure 3. Dependence of the dissociation yield β of SiHCl_3 molecules on parent pressure p_{TCS} for $\Omega_{\text{las}} = 797 \text{ cm}^{-1}$ and $E_{\text{las}} = 35 \text{ mJ}$.

polymer precipitate on the cell window with a common formula of the type $(\text{SiCl}_2)_n$. This conclusion is confirmed by the results of earlier investigations on thermal [20–22] and laser [23] pyrolysis, according to which the main channel of dissociation of SiHCl_3 molecules is the molecular elimination of HCl and the formation of SiCl_2 radicals followed by their rapid polymerisation.

Because it was quite difficult to carry out an isotopic analysis of the polymer precipitate, we tried to obtain the dissociation product in the form of a volatile compound. For this purpose, oxygen under a pressure of 5–20 Torr was added to trichlorosilane. It was found, however, that the excitation of, say, the mixture $\text{SiHCl}_3:\text{O}_2 = 1:20$ Torr, no dissociation products could be detected on account of the limited sensitivity of the recording technique. If, however, the pressure of SiHCl_3 was higher than 2–3 Torr, the material was consumed almost entirely during a single laser pulse, accompanied by a flash in the cell volume, pointing towards a branching mechanism of the photochemical reaction occurring in the cell. This conclusion was drawn from a comparison of the nature of the reaction and the set of the reaction products with the results of old experiments on thermal and photochemical oxidation of SiHCl_3 [26].

3. Conclusions

In this work, we have studied the IR multiphoton dissociation of SiHCl_3 molecules caused by pulsed irradiation by CO_2 and NH_3 lasers.

Our experiments have shown that pulsed CO_2 laser excitation into the overtone and composite vibrational bands leads to the dissociation of SiHCl_3 molecules, but this requires a high radiation energy density ($\sim 50\text{--}80 \text{ J cm}^{-2}$). Therefore, this excitation method seems to be rather inefficient from the point of view of silicon isotope separation.

The dissociation of trichlorosilane by NH_3 laser radiation seems to be more promising. First, the dissociation efficiency of this molecule is quite high: the dissociation threshold under conditions close to the collision-free regime is rather low (no more than 3 J cm^{-2}), so that a dissociation yield of several percent can be attained for moderate energy densities ($4\text{--}6 \text{ J cm}^{-2}$). Second, although deformation vibrations of the Si–H bond are used for exciting SiHCl_3 , a silicon isotopic shift may appear in it.

The dependence of the MPD yield on SiHCl_3 pressure can be used to estimate the limit beyond which dissociation

occurs in almost collisionfree regime. It is characterised by the parameter $p_{TCS}\tau_p < 1 \mu\text{s Torr}$, where p_{TCS} is the SiHCl_3 pressure, and τ_p is the total laser pulse duration.

The main final dissociation products of SiHCl_3 are HCl and a precipitate, presumably with the common chemical formula $(\text{SiCl}_2)_n$, which is in accord with the earlier investigations on thermal and laser pyrolysis of trichlorosilane.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research in association with the Ministry of Science and Industry of the Moscow region (Grant No. 01-03-97013), as well as by the Swiss National Research Foundation (Programme SCOPES 2000, Project No. 7SUPJ062201).

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