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Infrared Laser Chemistry of Trichlorosilane in View of Silicon Isotope Separation

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With a view toward laser isotope separation of Si, we have studied infrared multiphoton dissociation (IRMPD) of room temperature trichlorosilane, $SiHCl_3$. Over the wavelength range investigated, multiphoton dissociation of the room temperature species exhibits a maximum efficiency at 12.6 μm and a threshold fluence of only ∼1 J/cm^2. Vibrational overtone preexcitation of $SiHCl_3$ to the first SiH-stretch overtone ($2\nu_1$) prior to IRMPD results in a 10-fold increase of the dissociation yield compared to molecules with only thermal excitation. In an effort to collect the nascent $SiCl_2$ dissociation fragments, we have tested a number of different molecules that could serve as a scavenger to convert them into a stable gaseous compound. Several of these molecules react directly with trichlorosilane after being decomposed by collisional energy transfer from vibrationally excited $SiHCl_3$ and therefore are not suitable for a laser isotope separation process. Of the compounds tested, we find that only BCl_3 scavenges $SiCl_2$ without significant reaction with the starting material.

I. Introduction

The large increase in thermal conductivity of silicon upon isotopic purification[1] and the predicted unique properties of silicon isotope superlattices[2] suggest significant improvement of semiconductor devices upon use of isotopically enriched Si. Producing isotopically pure semiconductors is, however, currently limited by the high cost of enrichment. The development of economically feasible approaches for isotopic enrichment of these materials would facilitate exploring their potential in practical devices. The method of molecular laser isotope separation (MLIS) based on infrared multiphoton dissociation (IRMPD) has been investigated for the last three decades and applied to many isotopes, and recently it has been implemented for commercial production of carbon-13.[3] While isotope separation of silicon by IRMPD of naturally abundant (92.1% ^{28}Si, 4.7% ^{29}Si, 3.2% ^{30}Si) samples of $Si(OCH_3)_4$ and $((CH_3)_3Si)_2O$,[4] CH_3SiF_3, and $C_6H_5SiF_3$ [5] has achieved a maximum enrichment in ^{30}Si of only 5−15%, this approach has shown some promise for laboratory-scale separation of silicon isotopes using Si_2F_6 as a working molecule,[6−8] with a reported enrichment of ^{30}Si to 46% in the SiF_4 dissociation product[6] and 20% ^{29}Si in the SiF_2 fragment.[8] Although this is currently the most advanced laser-based technique for silicon isotope separation, the present level of enrichment is still far below that required for electronic applications.

A new highly selective MLIS approach based on overtone preexcitation of a high frequency vibration followed by IRMPD of the preexcited molecules has been recently proposed and studied in view of separating carbon[9] and silicon[10] isotopes. In both cases, this approach has achieved high isotopic selectivity, allowing enrichment of minor isotopes up to 99% in a single-stage process. For carbon isotope separation, this new technique has been applied to CF_3H, which as a symmetric top has a sharp, prominent Q-branch in the C−H stretch overtone bands, allowing efficient preexcitation of the parent molecules. In the case of silicon, this approach has been tested with SiH_4, a spherical top with a broad Q-branch in the Si−H overtone bands and a low density of vibrational states. These characteristics, along with the low pressure used in these experiments, resulted in a fairly low estimate for the productivity. To separate silicon isotopes successfully using the overtone-preexcitation infrared multiphoton dissociation (OP-IRMPD) approach, one must find a more suitable parent compound.

We report here our investigation of the applicability of the OP-IRMPD technique to the molecule trichlorosilane ($SiHCl_3$). This molecule is a good candidate for such an approach in that it has a light atom stretch vibration for overtone preexcitation (ν_1) that exhibits a sharp, ∼1 cm^{-1}, Q-branch.[11,12] In the minor isotopic species the Q-branch has been assigned only for the fundamental transitions.[13] Extrapolation of these data to the first overtone suggests ∼2.6 cm^{-1} isotopic shift per mass unit. The $2\nu_1$ Q-branch in the $^{29}SiHCl_3$ may partially overlap with a "hot" band, while the position of this branch in the ^{30}Si species should allow a significant isotopic selectivity of the preexcitation, especially at low temperatures, when the "hot" bands are substantially supressed. The particular selectivity figures for different preexcitation conditions have to be determined experimentally, perhaps with isotopically enriched $SiHCl_3$. In this work we use IRMPD of naturally abundant $SiHCl_3$ molecules vibrationally preexcited to the first Si−H stretch overtone to determine optimal parameters for selective dissociation of these species relative to the ground-state molecules, since this puts an upper limit for the isotopic selectivity of the process. Performing isotope-selective dissociation of the parent molecule is necessary but not sufficent for a successful isotope separation scheme, however. As in any MLIS process, the dissociation fragment(s) generated by IRMPD carrying the isotope of interest,

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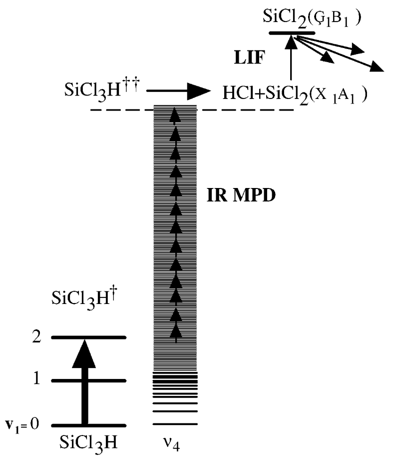

Figure 1. Schematic energy level diagram for infrared multiphoton dissociation of vibrationally excited $SiHCl_3$ followed by LIF detection of $SiCl_2$.

which in the present case is $SiCl_2$, must be collected and separated from the parent compound. The main reaction pathway for these radicals is formation of solid polymers of the type $(SiCl_2)_n$. Collection of this polymeric material would be inconvenient. The use of scavengers to convert radical products of chemical reactions into stable gaseous compounds has already been demonstrated in MLIS experiments.[14,15] In the second part of this work, we test the use of several potential scavenger molecules to collect the IRMPD products of $SiHCl_3$.

II. Experimental Section

Studies of $SiHCl_3$ dissociation by thermal[16−18] and laser[19] pyrolysis suggest that the lowest energy decomposition channel for trichlorosilane in the electronic ground state is the production of $SiCl_2$ and HCl:

$$SiHCl_3^{\dagger\dagger} \rightarrow SiCl_2 + HCl \qquad (1)$$

Under certain conditions, the $SiCl_2$ radicals polymerize to form $(SiCl_2)_n$.[17,18] We measure in situ the *relative* dissociation yield of reaction 1 after IRMPD using laser-induced fluorescence (LIF) detection of $SiCl_2$ immediately after the dissociation laser pulse. To measure the absolute IRMPD yield of $SiHCl_3$, we monitor its change in concentration by direct absorption after a known number of irradiation pulses.

Figure 1 shows a schematic energy level diagram for IRMPD of vibrationally excited $SiHCl_3$ followed by LIF detection of $SiCl_2$. First, an IR laser pulse excites the first overtone band ($2\nu_1$) of the Si−H stretch vibration. Approximately 400 ns later, a pulse from an NH_3 laser promotes some fraction of the vibrationally excited molecules to energies above the dissociation threshold via infrared multiphoton excitation of the ν_4 bending vibration. The $SiCl_2$ dissociation fragments are then detected by a third laser via LIF 600 ns after the preexcitation pulse. By choosing properly the dissociating frequency and fluence, one can dissociate selectively the preexcited molecules without significant dissociation of the ground-state species.

The apparatus we employ for these experiments, depicted schematically in Figure 2, has been described in detail elsewhere.[20,21] Briefly, we generate 3−4 mJ of infrared radiation at 4450.5 cm^{-1} for excitation of the first Si−H stretch overtone by difference frequency mixing the output of a Nd:YAG pumped dye laser with the fundamental of the same pump laser in a $LiNbO_3$ crystal. As a dissociating laser we use either a home-built NH_3 laser pumped by a pulsed CO_2 laser or the CO_2 laser directly. The dissociating pulse from the NH_3 laser largely resembles the pumping pulse, exhibiting a 150−200 ns initial peak and a 3−4 μs long tail. Because we probe the $SiCl_2$ dissociation products by LIF after only the first 600 ns of the dissociating pulse, the parent molecules that we investigate have experienced only 32% of the total fluence.

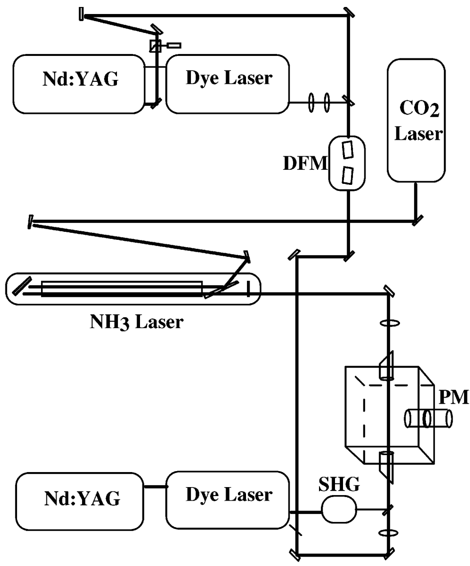

Figure 2. Apparatus for experiments on IRMPD of preexcited $SiHCl_3$.

For LIF detection of the $SiCl_2$ fragments at 325.084 nm (via the $\tilde{A}^1B_1$ (050) ← X $^1A_1$ (000) transition[22]), we use the second harmonic of another Nd:YAG-pumped dye laser. The probe laser beam is combined with the preexcitation beam on a dichroic mirror. The latter is focused by an $F = 60$ cm lens, resulting in 1.5 J/cm^2 fluence in the beam waist. The two beams are overlapped with the counter-propagating NH_3 laser beam, which is focused by an $F = 50$ cm lens to the center of the vacuum chamber. Semiconductor grade $SiHCl_3$ (Aldrich) slowly flows through the chamber at constant pressure.

In the second part of this work where we concentrate on product collection, experiments on IR-laser-induced chemistry of $SiHCl_3$ in the presence of different scavenger molecules have been performed in small (2.3- and 6.6-cm long) cells equipped with salt windows. The NH_3 laser beam is in this case focused by an $F = 10$ cm lens, resulting in a fluence of up to 10 J/cm^2 at the beam waist. Sharp focusing results in a significant variation of the dissociation fluence, and hence the dissociaion yield, along the length of the cell. For simplicity we use an average dissociation yield, β, to characterize the process. This yield is calculated from the attenuation of the IR absorption bands of $SiHCl_3$ measured in an IR spectrophotometer before and after laser irradiation of the cell. We employ the same technique, IR spectrophotometry, for identification and concentration measurements of the products of chemical reactions between scavenger molecules and the primary dissociation products of $SiHCl_3$. For this we record IR spectra of the gas mixture in the cell before and after irradiation by a certain number of ammonia laser pulses. The difference of the two spectra is compared with reference spectra of the expected chemical products. Most of these reference spectra have been taken from literature, although some of them have been obtained in our laboratory. We define the relative dissociation yield of a particular product as the ratio of its quantity to the quantity of the dissociated trichlorosilane.

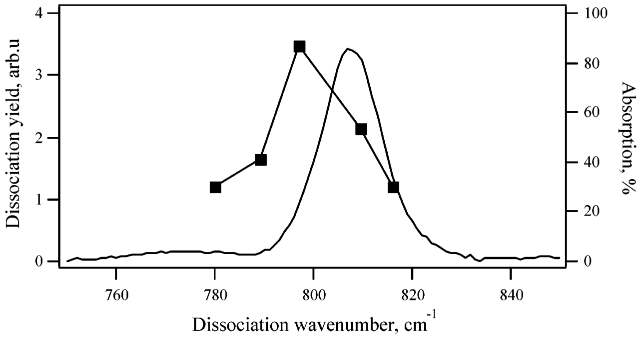

Figure 3. IRMPD yield for room-temperature $SiHCl_3$ as a function of the dissociation laser wavenumber (dots, connected by solid line). For comparison, an absorption spectrum of the ν_4 band in room-temperature $SiHCl_3$ is shown.

III. Results and Discussion

A. IRMPD of Room-Temperature and Vibrationally Preexcited $SiHCl_3$. Our first attempt at IRMPD of $SiHCl_3$ used excitation of the overlapped $2\nu_2$ and $\nu_4 + \nu_6$ bands[11] centered at 986 cm^{-1} by a CO_2 laser tuned to the 10R(20) and 10P(20) lines at 982.02 cm^{-1} and 944.18 cm^{-1}, respectively. Under these conditions, we detected a product LIF signal only when the effective dissociation fluence exceeded 20−30 J/cm^2 for a sample pressure in the range of 0.1−2.0 Torr. Such high dissociation threshold fluence is likely due to the low absorption intensity of the pumped band, making this scheme unsuitable for a practical isotope separation process. This led us to use an ammonia laser for pumping the strong ν_4 fundamental at 810.8 cm^{-1}. Figure 3 shows IRMPD yields measured for a few lines of the NH_3 laser using spectrometric detection of $SiHCl_3$ after the irradiation period. For comparison, an absorption spectrum of the ν_4 band is plotted on the same figure. The frequency of maximum yield is shifted by ~10−15 cm^{-1} to the low-frequency side from the maximum of the absorption spectra, prompting us to use the NH_3 laser lines below 780 cm^{-1} for IRMPD of vibrationally preexcited $SiHCl_3$.

The overall IRMPD efficiency of $SiHCl_3$ by the ammonia laser is significantly higher than that by the CO_2 laser. Despite the fact that the output energy of our ammonia laser on weak red lines (780, 773 cm^{-1}) is only 8−10% of the CO_2 laser energy, the dissociation yield is more than an order of magnitude higher than for direct dissociation of trichlorosilane by the latter. This suggests that infrared multiphoton excitation of trichlorosilane is 2 orders of magnitude more efficient when pumping through the ν_4 fundamental than that via the $2\nu_2/(\nu_4 + \nu_6)$ band. We thus concentrate on NH_3-laser-induced dissociation of $SiHCl_3$ in studying its suitability for isotope separation.

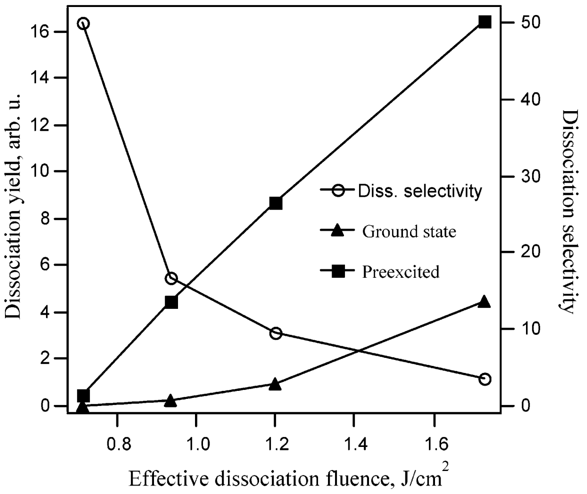

Figure 4. IRMPD yield as a function of effective dissociation fluence for room-temperature $SiHCl_3$ (triangles) and for $SiHCl_3$ preexcited to the $2\nu_1$ level (squares), left-hand scale. The dissociation selectivity, which is the ratio of the two yields, is also plotted as a function of the fluence (open circles, right-hand scale). The NH_3 dissociation laser is tuned to 780 cm^{-1}, and the sample pressure is 0.5 Torr.

Figure 4 shows the dissociation yield, measured by LIF detection of $SiCl_2$, as a function of the effective dissociation fluence for both vibrationally unexcited $SiHCl_3$ and for $SiHCl_3$ molecules preexcited to the $2\nu_1$ vibrational level. Dissociation of molecules in both vibrational states increases significantly with increasing fluence over the range investigated, but the increase is slower for the preexcited species, in line with our expectations.[20] An appreciable number of preexcited molecules dissociates at a fluence below 1 J/cm^2, where the dissociation yield from the room-temperature species is still small. The ratio of these two dissociation curves, which we call the dissociation selectivity, is plotted on the same figure (right-hand scale). Along with the isotopic selectivity of the preexcitation step, the dissociation selectivity as defined here limits the isotopic selectivity of the OP-IRMPD approach. We expect infrared multiphoton dissociation of the preexcited molecules to be isotopically selective, since the vibration that we use for IRMPE, ν_4, should also have some isotopic shift. We do not expect this selectivity to be significant, however, because the ν_4 absorption spectra of the two isotopic species in vibrationally preexcited room temperature molecules are strongly overlapped due to both rotational structure and vibrational statistical (inhomogeneous) broadening.[23] We can thus consider the dissociation selectivity plotted in Figure 4 as an estimate for the upper limit of isotopic selectivity in the overall OP-IRMPD process. At an NH_3 laser fluence of ~1.5 J/cm^2, where the dissociation yield of the preexcited $SiHCl_3$ is significant, this selectivity is only a factor of 5−6. This can be increased if one preexcites a higher fraction of molecules, but for an optical scheme with unfocused laser beams, which would be best from a practical point of view, the preexcitation fluence is limited to a few J/cm^2 because of the damage threshold of IR optical materials. Another way to increase the selectivity is to suppress the dissociation of the ground-state molecules and to favor that of the preexcited species by shifting the dissociation frequency further to the red from the ν_4 fundamental. Using the lowest frequency line available from our NH_3 laser (773 cm^{-1}) results in an almost 2-fold increase in dissociation yield of the preexcited molecules compared to a 25−30% drop in the dissociation yield of the ground-state species. As a result, this change of dissociation frequency increases the selectivity by a factor of ~2.5.

Figure 5 shows the dependence of the $SiCl_2$ LIF signals on $SiHCl_3$ pressure for both preexcited and room-temperature species dissociated by 1.5 J/cm^2 pulses of the ammonia laser tuned to 773 cm^{-1}. Because of collisional quenching of electronically excited $SiCl_2$, the LIF signal increases more slowly with pressure than the dissociation yield. The measured curves thus provide a lower limit for dissociation yield, especially for high pressure. However, since the change of LIF detection efficiency with pressure is the same for $SiCl_2$ produced by dissociation of ground-state and preexcited species, collisional quenching should not influence our measurements of dissociation selectivity, plotted in Figure 5 (right-hand scale). The selectivity reaches a maximum at ~0.5 Torr and then slowly drops with further increase of pressure, which is likely due to collisional vibrational deactivation of preexcited molecules. The initial increase of the selectivity can be explained by collisional rotational relaxation of a few states initially prepared by

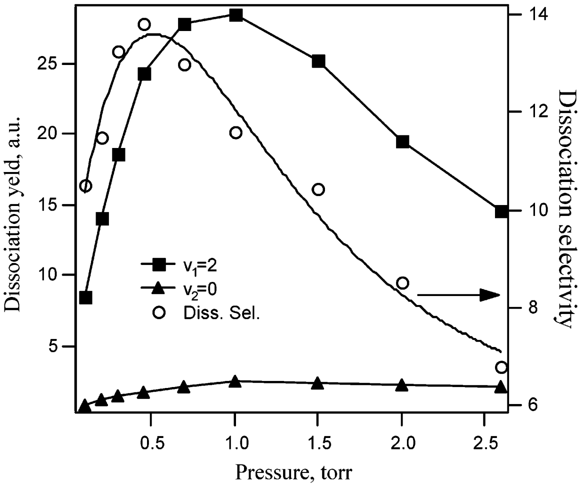

Figure 5. IRMPD yield as a function of $SiHCl_3$ pressure for the room-temperature molecules (triangles) and for the species preexcited to the $2\nu_1$ level (squares), left-hand scale. Dissociation selectivity, which is the ratio of the two yields, is also plotted as a function of pressure (open circles, right-hand scale). The NH_3 laser is tuned to 773 cm^{-1}, and the dissociation fluence is 1.5 J/cm^2.

preexcitation. This thermalization may populate rotational states that are favored for IRMPD by the 773 cm^{-1} laser line, leading to an increased dissociation yield for the preexcited species. A selectivity of around 10 reached for the sample pressure of 1−2 Torr implies, for example, a maximum possible isotopic enrichment of ^{29}Si species to 35%. If the preexcitation fluence were doubled it will be still below the damage threshold for IR optics, but should increase the level of enrichment to 50%.

The dissociation selectivity can be improved by cooling the molecules. Indeed, at room temperature, 82% of $SiHCl_3$ molecules have thermal excitation in low-frequency vibrations ($\nu_3 = 257.7$ cm^{-1}, $\nu_6 = 175.5$ cm^{-1}), giving rise to “hot” bands in the IR absorption spectrum of the ν_4. Multiphoton excitation through these “hot” bands may contribute significantly to dissociation of $SiHCl_3$ molecules without preexcitation. Lowering the working temperature will suppress this contribution and substantially increase the dissociation selectivity.

Collecting the $SiCl_2$ dissociation fragments in the gas phase requires the use of a scavenger molecule. Addition of a scavenger increases the working pressure and may influence the isotopic selectivity. In this regard, we have performed measurements of isotopic selectivity with He as a buffer gas. Addition of 9 Torr of He to 2 Torr of $SiHCl_3$ already decreases the selectivity by a factor of 5 due to an increased dissociation yield for the nonpreexcited molecules. In general, different collision partners will change this yield differently. Therefore, measurements of the selectivity should be performed for particular scavengers. Below, we report our results of a search for scavengers that could efficiently convert $SiCl_2$ fragments created by IRMPD to stable molecules, although we have not determined the selectivity achievable in the presence of these scavengers.

B. IR-Laser-Induced Chemistry of $SiHCl_3$. For IRMPD of room-temperature $SiHCl_3$ we employ an NH_3 laser tuned to the 797 cm^{-1} line with a dissociation fluence at the beam waist of 4−6 J/cm^2. Careful measurements show that the absolute IRMPD yield depends linearly on the sample pressure for pressures below 1 Torr. This implies that in this range, dissociation is not influenced by collisional effects (i.e., vibrational deactivation, rotational thermalization). We thus use a working pressure of 0.5 Torr whenever we want to ensure collision-free IRMPD. For sample pressures up to 10 Torr, the only gas-phase IRMPD product of pure trichlorosilane that we detect is HCl, in an amount equal to that of dissociated $SiHCl_3$. This is consistent with the lowest dissociation pathway for $SiHCl_3$, as described by eq 1. Over a long irradiation time we observe a solid deposit building up on the reactor windows, and its broad (~50 cm^{-1}) absorption band centered at 602 cm^{-1} suggests that this comes from $(SiCl_2)_n$ polymers. An efficient gas scavenger must therefore suppress the $SiCl_2$ polymerization and convert the radicals to a stable gas-phase product. Moreover, there are two additional requirements that a sucessful scavenger must meet in order to avoid scrambling the isotopic selectivity generated by the laser dissociation process—it should not react directly with the $SiHCl_3$ parent compound and it should not have an IR absorption band that overlaps with the frequency of the dissociation laser. Using the available chemical and spectroscopic data to judge their suitability, we selected a number of candidates for testing as scavengers of $SiCl_2$:

(a) di- and tri-atomics: O_2, CO_2, OCS;

(b) halogenated methanes: CH_2F_2, CF_4, CF_2Cl_2, CH_2Br_2, $CHBr_3$, CH_3I;

(c) others: C_2H_4, C_2F_4, BCl_3, $TiCl_4$, furan (C_4H_4O).

Each of these compounds has been mixed with trichlorosilane in the reaction cell and irradiated by the NH_3 laser, and the chemical composition of the reaction products were analyzed spectrophotometrically.

The laser-induced reaction of trichlorosilane with the smallest scavenger candidate, O_2, exhibits a characteristic threshold dependence on $SiHCl_3$ pressure. Irradiation of 20 Torr of O_2 with more than 4 Torr of $SiHCl_3$ results in a visible flash and complete disappearance of trichlorosilane after a single laser shot together with the formation of a film on the windows that exhibits broad IR absorption bands, which we attribute to silicon oxides. We also detect HCl, $(SiCl_3)_2O$, $SiCl_4$, and some nonidentified molecule(s) with a siloxane-type Si−O−Si bond. At $SiHCl_3$ pressure below 1 Torr, the bright flash disappears and the dissociation yield drops to ~0.7% per laser shot. We detect no gaseous products under these conditions. These results are similar to those from thermal and photochemical oxidation of $SiHCl_3$.[24] It is likely that at a sufficiently high $SiHCl_3$ pressure, the laser radiation vibrationally heats the molecules to a temperature above the threshold where the chain oxidation reaction occurs.

Tests of CO_2, OCS, CH_2F_2, CF_4, C_2F_2, and C_2F_4 did not reveal detectable gaseous products when 6−90 Torr is mixed with 6 Torr of $SiHCl_3$ and the latter is irradiated with the ammonia laser. Various stable gaseous products have been detected, however, after IRMPD of $SiHCl_3$ mixed separately with CF_2Cl_2, CH_2Br_2, $CHBr_3$, CH_3I, BCl_3, $TiCl_4$, and C_4H_4O. Table 1 summarizes these products for different mixtures of the tested scavengers with trichlorosilane. Among all the tested compounds, CF_2Cl_2 seems to be the best suited for scavenging $SiCl_2$ fragments. Irradiation of a mixture of CF_2Cl_2 with trichlorosilane favors formation of $SiCl_4$ and $SiFCl_3$, although several other compounds are also detected (Table 1). Figure 6 shows the yield of some of the detected products as a function of CF_2Cl_2 pressure. The yield of $SiCl_4$ is higher than the other products over the entire pressure range and at 60 Torr of CF_2Cl_2 reaches ~70% of $SiCl_3H$ dissociated by each laser shot in the cell irradiated volume. Thus, at CF_2Cl_2 pressures in this range, most of the $SiCl_2$ fragments are collected as a single chemical species.

Whether or not CF_2Cl_2 can be used for isotope separation depends on whether it scrambles significantly the isotopic selectivity of the overall process. This is largely determined by the mechanism of the $SiCl_2 + CF_2Cl_2$ reaction and by collisional

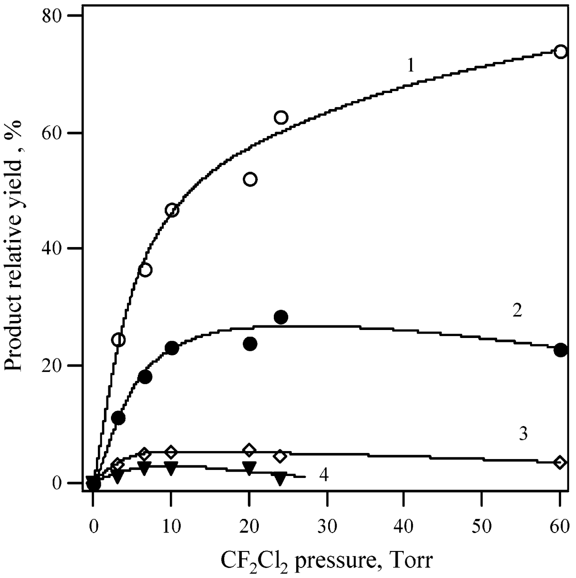

Figure 6. Yields of different gas products as a function of CF_2Cl_2 pressure in IRMPD of $SiHCl_3$ mixed with CF_2Cl_2: 1 (open circles) − $SiCl_4$, 2 (closed circles) − $SiFCl_3$, 3 (open squares) − SiF_2Cl_2, 4 (triangles) − SiF_3Cl. The yields are normalized to the dissociation yield of $SiHCl_3$ per each laser shot in the cell irradiated volume.

TABLE 1: IR Photolysis of $SiHCl_3$ Mixed with Different Scavengers

no.	scavenger	$SiHCl_3$ pressure, Torr	scavenger pressure, Torr	gaseous products
1	CF_2Cl_2	0.5	2−20	none
		6	3−60	$SiCl_4$, $SiFCl_3$, SiF_2Cl_2, SiF_3Cl, C_2F_4, HCl
2	CH_2Br_2	0.5	3	none
		6	4−36	presumably, $SiBr_{4-n}Cl_n$ $n = 1-3$, C_2H_4, C_2H_2, HCl
3	CH_3I	0.5	20	none
		4	20	presumably, $SiI_{4-n}Cl_n$ $n = 2-3$, C_2H_4, CH_4, HCl
4	BCl_3	0.5	5−27	$SiCl_3BCl_2$
		6	20−212	$SiCl_4$, $SiCl_3BCl_2$, HCl
5	$TiCl_4$	6	6−15	$SiCl_4$, presumably deposit of $TiCl_3$ and $TiCl_2$
6	C_4H_4O	0.5	15	C_2H_2, unidentified IR absorption band at 633 cm^{-1}
		2.5	18	C_2H_4, C_2H_2, unidentified IR absorption bands at 1304, 908, and 633 cm^{-1}

vibrational energy transfer processes. It is known that addition and insertion reactions are the main types of $SiCl_2$ radical reactions with stable compounds.[16] However, only with BCl_3 do we unambiguously find the insertion reaction product, $SiCl_3$-BCl_2 (Table 1), identified by its characteristic IR absorption spectrum.[25] The mechanism of reaction of $SiCl_2$ with other tested scavengers under laser radiation does not appear to be a simple addition or insertion. We suggest that a common feature of these reactions is the initial thermal decomposition of the scavenger during laser pulse via vibrational energy transfer from highly excited $SiHCl_3$. Indeed, with a typical V−V′ energy transfer rate[26] $k \sim 10^6\ s^{-1}\ Torr^{-1}$, a laser pulse duration $\tau \sim 10^{-6}$ s and a total pressure $p \sim 10$ Torr, the collisional exchange parameter, $k\tau p$, is approximately equal to 10. Under these conditions we expect substantial vibrational energy transfer from highly excited $SiHCl_3$ to other molecules. Moreover, a fraction of these species that do not reach dissociation threshold during laser pulse will dissipate their vibrational energy in post-pulse collisions. We believe that this transferred vibrational energy is sufficent to dissociate some fraction of the scavenger molecules. The importance of free radicals created by decomposition of a scavenger in binding $SiCl_2$ fragments is supported by the following experiments. First, an increase of a scavenger pressure (e.g., CF_2Cl_2 or CH_2Br_2) results in an increase in $SiHCl_3$ dissociation. Normally, the addition of a polyatomic gas results in a drop of dissociation yield due to collisional deactivation of the laser-excited species. In principle, the observed increase of dissociation yield could be explained by collisional refilling of a rotational bottleneck.[15] However, substitution of the scavengers with nonreactive Xe and N_2 at moderate pressures results in a reduced $SiHCl_3$ dissociation yield, despite the fact that these two gases are highly efficient for rotational relaxation.[15] This prompts us to conclude that rotational relaxation is not important at typical pressures of our experiments. Moreover, it leads us to suggest that the observed growth of the dissociation yield with increasing pressure of a scavenger could be due to the reaction of $SiHCl_3$ with fragments created by collision-induced decomposition of the scavenger. A second result in support of this suggestion is the observation that a high yield of the laser-induced reaction is observed only for the scavengers that have a dissociation limit near or lower than that of $SiHCl_3$ (D_0 = 72 kcal/mol[18]). It is simply difficult to dissociate a scavenger in collisions with molecules that have little vibrational energy.

Two more sets of experiments have been performed to clarify the mechanism of the laser-induced reaction. In one, vibrational heating of scavengers in collisions with $SiHCl_3$ has been strongly suppressed by lowering the pressure of trichlorosilane by more than an order of magnitude—down to 0.5 Torr. No gaseous products were detected under these conditions for any scavenger (see Table 1) except BCl_3, where we detect the same insertion product—$SiCl_3BCl_2$. In another experiment we have performed IRMPD of CF_2Cl_2 by a CO_2 laser through the lowest dissociation channel of these molecules:[15]

$$CF_2Cl_2 + nh\nu \rightarrow CF_2Cl + Cl \qquad (2)$$

These experiments were carried out under conditions where the CF_2Cl_2 pressure (0.35 and 0.7 Torr) is much smaller than that of $SiHCl_3$ (6 Torr). The $SiHCl_3$ molecules do not absorb radiation from the CO_2-laser, and collisional energy transfer from the small number of excited CF_2Cl_2 to $SiHCl_3$ is negligible. Therefore, trichlorosilane cannot dissociate under these conditions by either direct IRMPD or collisional heating from hot trichlorosilane. Nevertheless, IRMPD of CF_2Cl_2 in mixtures with $SiHCl_3$ results in an approximately equal consumption of both species, and it is equal to the yield of IRMPD for pure CF_2Cl_2 (reaction 2). The resulting gaseous products, $SiCl_4$, $SiFCl_3$, and C_2F_4, are the same as those detected upon IRMPD of 6 Torr of $SiHCl_3$ mixed with an excess CF_2Cl_2 (as discribed above).

Both results support our proposed mechanism of the laser-induced reaction of the investigated scavengers in mixtures with $SiHCl_3$. When more than 3−6 Torr of trichlorosilane in a mixture with a scavenger is irradiated by the ammonia laser, the excited $SiHCl_3$ heats and dissociates the scavenger in collisions. Dissociation fragments of the scavenger may react with $SiCl_2$ radicals or with the $SiHCl_3$ starting material, the latter of which will scramble the isotopic selectivity gained by laser overtone preexcitation of $SiHCl_3$. This leads us to conclude that at moderate trichlorosilane pressure, none of the tested compounds, and in particular CF_2Cl_2, can be used as an $SiCl_2$ scavenger in an IRMPD-based isotope separation process. At low trichlorosilane pressure (<0.5 Torr), however, the rate of scavenger reaction with the starting material becomes insignificant and products are formed typically by insertion of $SiCl_2$ radicals into a suitable scavenger bond. Such a reaction should not deteriorate isotopic selectivity gained at earlier stages (i.e., by overtone preexcitation followed by IRMPD) of the isotope separation process. Our estimate shows that at trichlorosilane pressures below 0.5 Torr, up to 40% of all available $SiCl_2$ fragments can be collected this way by inserting the fragments into a single B−Cl bond in BCl_3, forming $SiCl_3BCl_2$ molecules. However, the low pressure of $SiHCl_3$ together with a 60% loss of fragments still make the use of BCl_3 as a $SiCl_2$ scavenger in the overtone preexcitation-IRMPD isotope separation process questionable. Moreover, BCl_3 is highly undesirable if the enriched material is used in a semiconductor fabrication, where boron is one of the doping elements whose level must be controlled on a ppt level. More candidates should be tested to find an efficient scavenger for this process, preferably one that proceeds by a simple insertion reaction. In pre-selecting the candidates for such tests, one should keep in mind that $SiCl_2$ does not efficiently insert into C−F, C−Cl, C−Br, C−I bonds. On the basis of the known value for the $SiCl_2$ polymerization rate,[25] together with the concentration of $SiCl_2$ and the pressure of scavengers in our experiments, we estimate an upper limit for the rate of insertion into these scavengers to be 2×10^{-17} cm^3/s.

IV. Conclusions

With a view toward developing the overtone preexcitation-IRMPD approach for highly selective laser isotope separation of silicon, we have studied IRMPD of $SiHCl_3$ and subsequent reactions of the $SiCl_2$ dissociation fragment with potential scavengers of these fragments. The dissociation of room-temperature $SiHCl_3$ by a CO_2 laser via the weak $2\nu_2/(\nu_4 + \nu_6)$ band turns out to be inefficient, with a high (20−30 J/cm^2) dissociation fluence threshold. The dissociation becomes 2 orders of magnitude more efficient and the fluence threshold drops below 1 J/cm^2 if one pumps the strong ν_4 fundamental by an ammonia laser. The spectral maximum of the IRMPD yield appears at $\sim$795 cm^{-1}.

The dissociation efficiency increases even further when $SiHCl_3$ molecules are preexcited to the $2\nu_1$ overtone level. At sample pressures of 1−2 Torr, and preexcitration fluence of $\sim$1.5 J/cm^2 the dissociation yield of the preexcited molecules is an order of magnitude higher than that of the room-temperature species. This result, if scaled to practically realistic laser parameters of lasers, should result in an enrichment of the minor Si isotopes in the $SiCl_2$ dissociation fragments of up to 50%. Lowering the temperature will suppress the ν_4 "hot" bands and may significantly improve this number.

Given this high degree of selectivity in the excitation process, we have performed an extensive search for a suitable scavenger for the $SiCl_2$ fragments. At moderate pressures of $SiHCl_3$, we have found that almost all tested scavengers react directly with trichlorosilane after being activated by collisional energy transfer from vibrationally excited $SiHCl_3$. This reaction will scramble isotopic selectivity of the process. At low $SiHCl_3$ pressure where collisional heating is suppressed, the main pathway of the reaction is an insertion of $SiCl_2$ into a suitable bond of the scavenger. We have found that at pressures below 0.5 Torr, BCl_3 reacts with $SiCl_2$ fragments in this way, forming $SiCl_3BCl_2$. At the same time we do not observe evidence for a direct reaction of BCl_3 and $SiHCl_3$, allowing this compound to scavenge $SiCl_2$ without scrambling isotopic selectivity. Our estimate shows that BCl_3 can scavenge at most 40% of all $SiCl_2$ fragments. Together with the relatively low sample pressure (<0.5 Torr), this low collection efficiency would limit substantially the productivity of the isotope separation process and make the use of BCl_3 as a scavenger questionable.

The use of our overtone-preexcitation IRMPD approach to MLIS of Si with $SiHCl_3$ as a parent molecule remains dependent on finding an efficient scavenger for $SiCl_2$. Additional compounds can be tested for this purpose, keeping in mind the constraints described here, although the combination of a high rate of $SiCl_2$ polymerization and high $SiHCl_3$ reactivity makes this problem difficult to solve. Alternatively, one may collect $SiCl_2$ via polymerization, since during this process $SiCl_2$ does not react with the starting material[31] and, therefore, it should not scramble the isotopic selectivity.

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