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Collisional effects in the IR multiphoton absorption and dissociation of Si_2F_6

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Abstract

IR multiphoton absorption (MPA) and dissociation (MPD) of Si_2F_6 in Ar were investigated. For the 10R(26) line (979.7 cm^{-1}) of the CO_2 laser, the average number of photons absorbed and the MPD yield were obtained for different laser fluences and buffer gas pressures. The fraction of excited molecules was as high as 70%. The MPD probability was found to be heavily suppressed when more than 5 Torr of Ar buffer gas was added, indicating that vibrational deactivation is predominant over MPA increase with pressure.

Keywords: Hexafluorodisilane; Multiphoton absorption; Multiphoton dissociation; Laser isotope separation

1. Introduction

Pulsed radiation from a CO_2 laser induces efficient IR multiphoton absorption (MPA) in the Si_2F_6 ν_7 normal mode [1–4]. Subsequent multiphoton dissociation (MPD) has been investigated as a potential method for Si isotope separation [1,2] and as the most efficient way of generating the SiF_2 long-lived radical [3,4]. The MPD process has recently been established [4] to be straightforward: the simultaneous formation of SiF_4 and SiF_2 has confirmed that the reaction $Si_2F_6 \rightarrow SiF_4 + SiF_2$ is the main channel of dissociation. The reaction rates of SiF_2 with Br_2, NO_2 and C_2H_4 have been measured in Ref. [4] by time- resolved IR diode spectroscopy.

However, in contrast with SF_6 which has been studied extensively, little is known about the vibrational spectroscopy and multiphoton excitation process of the Si_2F_6 molecule. For this reason, we have begun a systematic study of the spectroscopy and interaction dynamics with the laser photon field of this molecule. Measurement of the FTIR and Raman spectra [5] at room temperature has provided improved values of the frequencies for all normal modes, including the previously unknown torsional frequency and the barrier to internal rotation. The jet-cooled high-resolution diode laser spectra of the ν_5 parallel [6] and ν_7 perpendicular [7] bands of the Si_2F_6 major isotopomers have yielded precise values for the band origins, rotational constants, Coriolis constants and isotopic shifts. Very recently, we have reported [8], for the laser lines from 10R(10) to 10R(38), the number of photons absorbed per molecule and the average MPA cross-sections for neat Si_2F_6. The dependence on the laser frequency revealed a large anharmonic shift in the MPA maximum, which was explained as a combined effect of the ν_7 mode anharmonicity and the hot- band contributions to MPA. Indeed, Si_2F_6 has many low-lying vibrational levels which are largely populated at room temperature, and therefore multiphoton transitions starting from these levels will enhance and shift towards the red the MPA maximum.

In this study, we investigate the influence of the buffer gas pressure on MPA, determining the extent of the rotational bottleneck effect for different laser fluences. In addition, we measure the Si_2F_6 MPD probability as a function of the laser fluence and buffer gas pressure. The laser line used for irradiation was 10R(26), which is slightly red shifted relative to the above-mentioned MPA maximum and, consequently, MPD will also take place efficiently.

2. Experimental details

Si_2F_6 gas was prepared as described elsewhere [5] by fluorination of Si_2Cl_6. The final product contains SiF_4 as an impurity, but most can be separated by distillation, so that the concentration of SiF_4 in Si_2F_6 gas is less than 2%.

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The basic experimental conditions for both MPA and MPD experiments were the same. Mixtures of 0.1 Torr of Si_2F_6 and 0–600 Torr of Ar buffer were used in static cells at room temperature. MKS Baratron vacuum gauges in the pressure regions 10, 100 and 1000 Torr were used to achieve accurately the desired composition of the mixture. The mixture was allowed to become homogeneous before measurement. Preliminary leak and dark tests confirmed that the amount of Si_2F_6 can be regarded as unchanged during the measurements. In an unfocused irradiation geometry, the maximum fluence delivered by the Lumonics 103 TEA-CO_2 laser was 0.5 J cm^{-2}. A mixture of He and CO_2 (6 : 1) was used for the CO_2 laser. The temporal profile of the laser pulse, measured with a photon-drag detector (Hamamatsu), shows a pulse duration $\tau_p = 100$ ns full width at half-maximum (FWHM) with no tail. For 0.1 Torr of neat Si_2F_6 gas, the average time between collisions is 1.5 μs at room temperature, which is much longer than τ_p; therefore we can assume that collisionless conditions hold. By adding buffer gas, we can vary the condition of absorption from collisionless to collisional.

For MPA measurements, we used a cross-shaped stainless steel cell with arms of 80 cm and 10 cm equipped with CsI and KBr windows respectively on their ends. The short arm allowed us to measure the FTIR spectrum and to check the initial conditions. The fluence was varied from 10 to 500 mJ cm^{-2} using various combinations of CaF_2 attenuators. We did not consider the change in beam fluence along the cell, although a maximum of 25% of the incident energy is absorbed by the gas in the cell. It has been shown elsewhere that, in this kind of measurement, the error arising from not considering the change in fluence along the cell is within 2% even if as much as 40% of the incident energy is absorbed [10].

In the MPA measurements, it was necessary to avoid the influence of MPD, which changes the composition of the gas in the cell. Even when the MPD rate is small, it is desirable to minimize the number of shots necessary for the measurement. For each fluence, we irradiated the cell with only one laser shot and measured the pulse energy of both the incident and transmitted beams with two pyroelectric detectors placed in front of the cell via a beam splitter and after the cell. We went from low to high fluence and repeated this procedure three times successively. The data for each run were practically the same, showing that the influence of MPD is small in this experiment.

For MPD measurement, we used a stainless steel cell 10 cm in length with KBr windows on both ends. The fluence was varied from 0.1 to 2 J cm^{-2} by placing CaF_2 attenuators of different thickness before the cell and by using two confocal BaF_2 lenses (focal lengths, 40 cm and 20 cm). We also monitored the transmitted beam with a pyroelectric detector so that we could skip incomplete laser pulses. After irradiation with a number of pulses, which was varied depending on the fluence, we measured the FTIR absorption spectrum (Perkin Elmer 1600 series FTIR, resolution 4 cm^{-1}). The amount of Si_2F_6 remaining in the cell is proportional to the integrated absorption of the ν_7 band. In the MPD experiment, the number of remaining Si_2F_6 molecules in the cell after n laser pulses (N_n) follows the relation, $N_n/N_0 = (1 - rq)^n$, where r is the ratio of the interacting volume to the volume of the cell and q is the MPD probability defined as the fraction of molecules dissociated by one laser pulse. The parameter r is introduced in order to correct for the effect of dilution of the irradiated part of the gas by the unirradiated part of the gas. The ratio of the area of the ν_7 band after n pulses to the initial area of this band as a function of n gives a straight line in a semi-logarithmic plot, indicating that the above-mentioned relation holds. From the slope of the plot, the MPD probability for each fluence can be obtained. The feasibility of this method was checked by comparing the integrated absorption of ν_5 (824 cm^{-1}) and ν_7 bands of Si_2F_6. They were always proportional to each other. We also checked that the ν_3 integrated absorption of SiF_4 (band origin at 1030 cm^{-1}) increased consistently in accordance with the decomposition of Si_2F_6.

3. Results and discussion

3.1. MPA

As previously [8], we compared different MPA data by representing in a log–log plot the average number of photons absorbed $\langle\langle n\rangle\rangle$ as a function of the normalized fluence $\sigma_0\Phi$, where σ_0, the spectroscopic absorption cross-section, was obtained for each partial Ar pressure as described in Ref. [8]. For selected values of the Ar pressure, these data are plotted in Fig. 1. As can be seen, if only 0.1 Torr of Si_2F_6 is present,

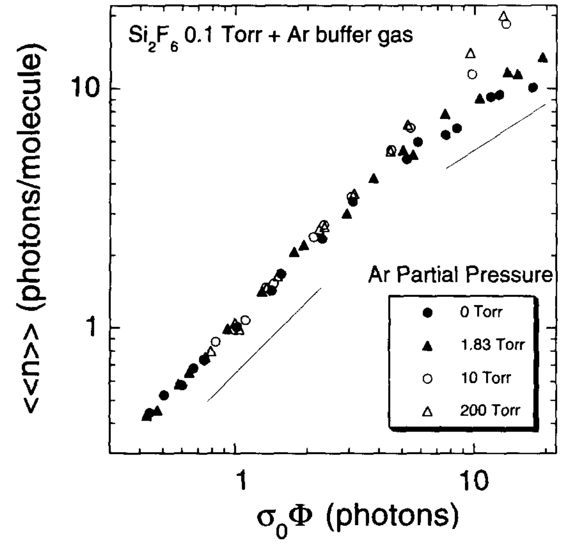

Fig. 1. Average number of absorbed photons as a function of laser fluence and for different Ar pressures. The fluence is normalized by the absorption cross-section for each composition of the mixture which was obtained as described in Ref. [8]. The cross-sections are 6.2×10^{-18}, 7.5×10^{-18}, 8.6×10^{-18} and 8.5×10^{-18} cm^2 for 0, 1.83, 10 and 200 Torr of total pressure respectively. The lines with slopes of unity and two-thirds are shown.

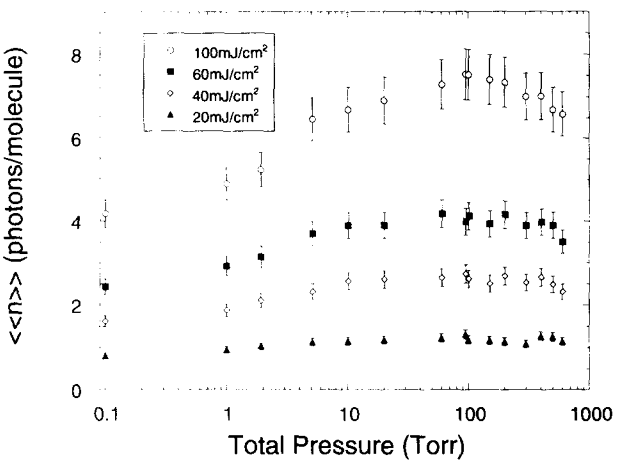

Fig. 2. Average number of absorbed photons as a function of total pressure and for the laser fluences indicated in the figure. The partial pressure of Si_2F_6 is 0.1 Torr. The absorption by the window is corrected for.

the slope in the low-fluence region is unity and decreases towards two-thirds as the fluence increases. This result was also obtained [8] for other laser lines and fits well with the general MPA behaviour of polyatomic molecules [11]. The change in the slope can be understood by assuming that the absorption cross- sections $\sigma_{n+1,n}$ decrease for the high vibrational levels close to the dissociation limit. It is generally accepted in the theoretical models of MPA based on rate equations that $\sigma_{n+1,n}$ is a decreasing function of n, but the specific function differs from model to model [12]. On addition of the buffer gas, the slope in the low-fluence region is not affected, but it increases in the high-fluence region. For Ar pressures higher than 10 Torr, a slope of unity is observed over the whole fluence range. This effect is also consistent with the above-mentioned assumption on the cross-section. In the presence of buffer gas, the molecules remain in lower vibrational states due to efficient vibrational deactivation. For these states, the absorption cross-section does not vary significantly from level to level and MPA is linear for a wider range of fluences.

As shown in Fig. 2, $\langle\langle n\rangle\rangle$ increases with Ar pressure, especially for lower Ar pressures. The enhancement of absorption can be attributed mainly to rotational hole filling. Molecules interact only with other molecules which are in favourable rotational states, therefore only part of the molecules can be excited (rotational bottleneck). If collisions occur during the laser pulse, the fraction of the interacting molecules increases by rotational relaxation and this bottleneck can be overcome (rotational hole filling). A broadening of the vibrational levels and a collisionally enhanced intramolecular V–V energy transfer [13] also increase absorption; however, it is reasonable to assume that rotational hole filling is the main cause of the absorption enhancement because, as shown later, the time constant obtained from a fit of the data gives a value (200 ns Torr) which is more likely to be a rotational relaxation time. In addition, numerical simulation based on the rate equations, which is not described in this report, reproduces these data well by only considering rotational relaxation. Another reason is that rotational hole filling can easily explain such a clear saturation. Saturation takes place around 100 Torr and the shape of the curve is similar for all fluences. For larger fluences, however, the curve saturates more slowly which is again consistent with a decrease in $\sigma_{n+1,n}$ with n.

Since the saturation is very clear, we can assume that the fraction of collisionless excited molecules is simply the ratio of the number of photons absorbed in neat Si_2F_6 to the saturated value [14]. Usually the fraction itself depends on the fluence, so we extrapolated the ratio to the low-fluence limit and obtained the fraction of accessible molecules by this laser line to be about 70% for 0.1 Torr of neat Si_2F_6. The high rotational density of states, combined with the enhancement of absorption by the hot-band transition, must be responsible for this large value of the fraction of excited molecules. Indeed, for Si_2F_6, the small rotational constants [6,7] generate a dense structure of (J,K) levels. Only $\Delta K = \pm 1$ transitions are allowed for the ν_7 fundamental, but for higher vibrational transitions within the ν_7 mode and for hot-band transitions both $\Delta K = \pm 1$ and $\Delta K = 0$ are allowed. This increases considerably the number of excitation paths in the multiphoton transitions.

Although it is not possible to obtain the rotational relaxation time [14] directly from the above results, it is worth obtaining the phenomenological parameter $p\tau_{\mathrm{rot}}$ for hole filling. The rising part of Fig. 2 is well expressed in terms of an exponential curve, $[1-\exp(p/p_0)]$, where p is the total pressure and p_0 is a constant. For 15 mJ cm^{-2}, a least-squares fit of the data yields $p_0 = 2$ Torr. At this pressure, the characteristic time for rotational hole filling and the pulse duration are of the same order; thus for the Si_2F_6–Ar system, $p\tau_{\mathrm{rot}} = 200$ ns Torr is obtained.

When we add more Ar buffer gas ($p > 100$ Torr), the number of photons absorbed apparently decreases. To our knowledge, this fact has not been discussed elsewhere. The reason for the decrease is not clear at this point. A similar result for SF_6 with buffer gas was obtained in a computer calculation of MPA using rate equations [15], but no direct explanation was given.

In order to check whether there is a laser intensity effect on MPA, we measured $\langle\langle n\rangle\rangle$ with long pulses of the same fluence, which were produced using N_2 gas in a mixture of CO_2, N_2 and He (1 : 1 : 6) for the TEA-CO_2 laser system. In this case, the laser pulse has a 100 ns spike and a tail of 2 μs duration, so for the same fluence the intensity is lower. The result is shown in Fig. 3. It can be seen that, for equal fluences, the number of absorbed photons is larger for longer pulses (lower intensity). The ratio of $\langle\langle n\rangle\rangle$ for short to long pulses is about 0.7, and this small difference suggests that the intensity effects play a small role in MPA in this case. Since this ratio is close to the fraction of excited molecules, it is probable that the increase is due to rotational hole filling during the long laser pulse. We cannot exclude the possible contribution from V–V energy transfer: although this is normally slower

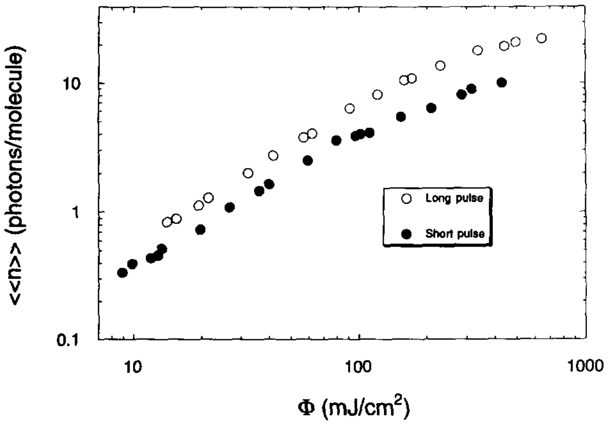

Fig. 3. Average number of absorbed photons in 0.1 Torr of neat Si_2F_6 gas as a function of the laser fluence for two different laser pulses: ○, long pulses (100 ns spike + 2 μs tail); ●, short pulses (100 ns).

than rotational relaxation, Si_2F_6 has many low vibrational levels and V–V transfer processes take place with higher probabilities.

3.2. MPD

The MPD probability obtained for 0.1 Torr of neat Si_2F_6 is represented in Fig. 4 as a function of fluence. At low fluence, the MPD probability is very small, but it increases rapidly and asymptotically approaches unity. The fluence necessary to dissociate 1% of the molecules is around 0.25 J cm^{-2} for these experimental conditions. This confirms the ease of decomposition of Si_2F_6, which can be attributed partly to the low bond dissociation energy, and partly to the high excitation efficiency of this molecule, as discussed above.

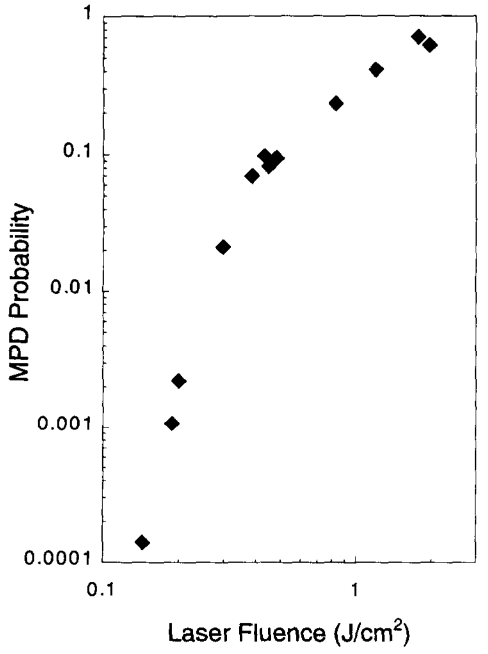

Fig. 4. MPD probability of neat Si_2F_6 gas (0.1 Torr) as a function of the laser fluence.

The effect of buffer gas on MPD is shown in Fig. 5 where the MPD probability is plotted as a function of the total pressure at a fluence of 1.6 J cm^{-2}. We can see that the dissociation is heavily suppressed when more than 5 Torr of Ar is added, so that for pressures higher than 50 Torr it is less than 1%. These data clearly show that there is competition between the favourable factor due to rotational hole filling and the unfavourable factor due to collisional deactivation. As can be seen from Fig. 2, $d\langle\langle n\rangle\rangle/dp$ is almost saturated for $p < 5$ Torr; thus it seems that in this range of pressures the two opposing effects are roughly in equilibrium. The high fraction of collisionless excited molecules naturally limits the extent of rotational hole filling: if 70% of the molecules are already excited at 0.1 Torr of neat gas, adding Ar can only bring the remainder to excitation.

Now that we have obtained the MPD data, we can check whether the dissociation affects the results of the MPA measurements. Using the results shown in Fig. 4, we estimated that the total fraction of dissociated molecules during one MPA measurement is about 3%, which is sufficiently small to be ignored. This is consistent with the fact that the differences in the MPA data in two successive runs were small.

It is worth evaluating the time constant τ_v for the decrease in the dissociation probability from Fig. 5. The curve in Fig. 5 fits well with a simple exponential, $q = q_0\exp(-p/p_0)$, where q is the dissociation probability. From the least-squares fit in Fig. 5, $q_0 = 0.62$ and $p_0 = 31$ Torr were obtained. This decrease is expected to be related to the number of collisions during the laser pulse; therefore the characteristic parameter $p\tau_v = 3.1$ μs Torr is obtained. In the absence of any data on

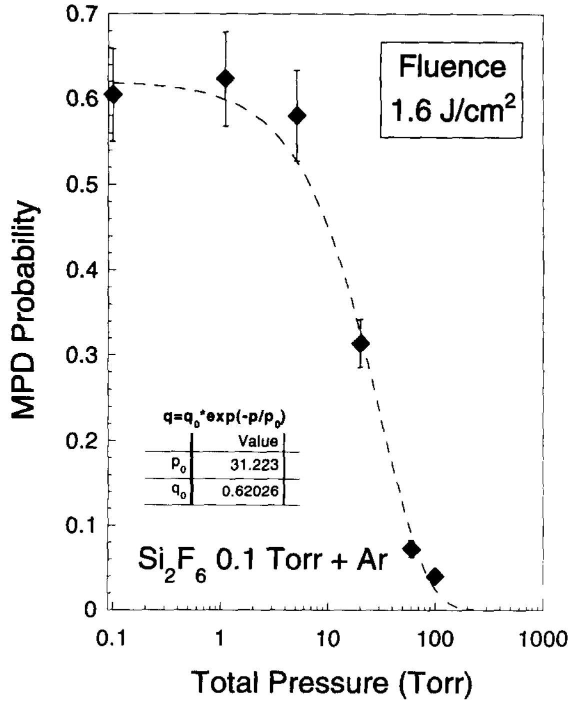

Fig. 5. Dissociation probability of Si_2F_6 gas (0.1 Torr) as a function of the Ar pressure at a laser fluence of 1.6 J cm^{-2}. The parameters of the exponential fit are also presented.

Si_2F_6 vibrational relaxation, we can assume that the vibrational relaxation rates will be of the same order of magnitude as $(p\tau_v)^{-1}$.

For total pressures less than 5 Torr, the MPD probability is not affected by collisions. We can therefore work up to this pressure without destroying the climbing of molecules towards dissociation. This is consistent with data on the isotopic selectivity obtained by Kamioka et al. [1]: irradiating neat Si_2F_6 gas at 951.2 cm^{-1} to decompose $^{28,30}Si_2F_6$, they observed a constant enrichment factor for ^{30}Si up to 5 Torr pressure, and a decrease for higher pressures. However, it should be noted that their relative yield for $^{28}SiF_4$ and $^{30}SiF_4$ is a decreasing function of pressure even for small pressure values. As they used neat gas, this difference might be attributed to the efficiency of collisional deactivation. Ar atoms are clearly less efficient collisional partners for Si_2F_6, while in the binary $Si_2F_6{}^*$–Si_2F_6 collisions the energy exchange is more efficient.

The present results, combined with previous data [8] on neat Si_2F_6, allow us to describe the behaviour of Si_2F_6 on interaction with pulsed laser radiation in more detail. The low- fluence MPA cross-section is almost equal to the spectroscopic absorption cross-section; also the MPA cross-section shows a weak dependence on the laser fluence. The MPD probability increases rapidly with fluence and approaches unity, as is evident from our data in Fig. 4. On the other hand, Si_2F_6 exhibits collisional enhanced absorption (demonstrated by the data in Fig. 2) and a sizeable red shift of the MPA spectrum [8]. Indeed, the red shift in the MPA spectrum can be partly attributed to the hot-band contribution. Also, the decrease in the MPA cross-section with laser fluence is weak, and the fraction of the rotational population absorbing the laser energy is large. Recent data on Si_2F_6 vibrational spectroscopy [5] directly support this. The low-frequency normal modes $\nu_9 = 153$, $\nu_{12} = 202$ and $\nu_3 = 218$ cm^{-1} and, especially, the torsional mode at $\nu_4 = 38$ cm^{-1} will produce a high density of vibrational states which will lower the onset of the quasicontinuum. The analysis of the high-resolution vibrational–rotational spectrum of the perpendicular ν_7 band of Si_2F_6 [7] revealed a local perturbation of the ν_7 levels, probably from a very close vibrational level of the same symmetry. This indicates that already at $\nu_7 = 1$ there exists a coupling of the ν_7 mode with the background of other modes. However, the vibrational density of states is not the only factor. The low-frequency modes also generate low-lying vibrational–torsional levels from which many hot-band transitions can start at room temperature. Finally, the large moments of inertia of the molecule will produce a dense structure of rotational levels. A high density of vibrational–rotational states, combined with many low- frequency modes to aid anharmonic coupling, will certainly cause the high fraction of excitation of Si_2F_6 in MPA and MPD processes.

4. Conclusions

We performed MPA and MPD measurements of Si_2F_6 and $Si_2F_6 + Ar$ mixtures with TEA-CO_2 laser pulses of 100 ns width at a wavelength of 10.21 νm.

In the MPA experiment, the dependence of the average number of photons absorbed on the fluence and the Ar partial pressure was studied. The fraction of interacting molecules for 0.1 Torr of neat Si_2F_6 gas was about 0.70; thus it was directly confirmed that the rotational bottleneck is not significant for this molecule. The fluence that gives 1% MPD probability is 0.25 J cm^{-2} in a collision-free condition. When more than 5 Torr of buffer gas was added, the MPD probability decreased drastically. Analysing the dependences of MPA and MPD on the buffer gas pressure, the time constants for rotational hole filling and vibrational deactivation for the Si_2F_6–Ar system were evaluated. In addition to the importance of a knowledge of their intrinsic values, these results may be used to optimize the scheme of selective multiphoton decomposition of the molecule with a view to the separation of Si isotopes by laser radiation.

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