

Isotopically Selective Dissociation of CCl_4 Molecules by NH_3 Laser Radiation

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Abstract. The IR NH_3 laser radiation was applied for selective dissociation of CCl_4 molecules. The dissociation yield, its pressure dependence and isotopic selectivity were measured. Two-frequency dissociation of CCl_4 by the NH_3 laser and the CO_2 pump laser radiations was carried out. It was shown that the NH_3 laser is very effective for CCl_4 dissociation.

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The multiple photon dissociation of polyatomic molecules by IR radiation is now believed to be the most promising method of laser isotope separation [1]. This is mainly due to the unique combination of power and efficiency of the TEA CO_2 lasers used. The CO_2 laser has a limited range of tunability, whereas the vibrational frequencies of many molecular compounds (especially containing heavy atoms) are in the region lower than 900 cm^{-1} which is inaccessible for CO_2 lasers. Therefore the future developments of isotope separation by multiple photon dissociation greatly depend on the creation of powerful, tunable and efficient lasers with frequencies from 400 to 900 cm^{-1} . One of the most effective methods of laser generation in this spectrum range is the optical pumping of molecules [2, 3]. The NH_3 laser developed a year ago [4] is rather promising. The output energy of this laser reached 0.35 J with a sufficient power level (up to 0.5 MW) and a high efficiency (up to 8% in energy) [5]. This result allowed to apply the NH_3 laser for multiple-photon dissociation.

This paper reports the unimolecular dissociation of CCl_4 molecule both by the NH_3 laser radiation and by simultaneous action of resonance (NH_3 laser) and off-resonance (CO_2 laser) radiation. The dissociation is found to be isotopically selective, the enrichment factors obtained for dissociation products are 4–6 for carbon isotopes ^{12}C and ^{13}C and 1.12–1.15 for chlorine isotopes ^{35}Cl and ^{37}Cl .

1. Experimental Technique

The set-up consisted of a TEA CO_2 pump laser, ammonia laser and a gas cell for CCl_4 (Fig. 1). The CO_2 laser cavity was formed by a spherical mirror M_1 and a grating G. The pulse energy at the R(16) line (1076 cm^{-1}) was 6 J with gas mixture of $\text{CO}_2}:\text{N}_2}:\text{He} = 1:1:4$. The energy was extracted from the cavity through the zero-th order of the grating and was directed into the ammonia cell of 1.6 m length without focusing. This cell had a KBr window and a spherical mirror M_2 at the other end. The NH_3 laser cavity was formed by mirrors M_1 , M_2 and a grating G and had a length of 4.5 m . The NH_3 laser radiation at $12.8\text{ }\mu\text{m}$ was extracted through the first order of the grating. Its

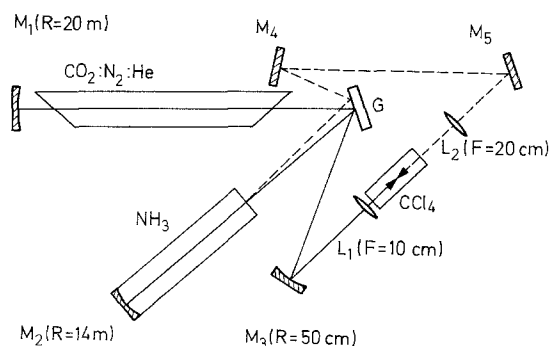


Fig. 1. The optical set-up (M_1, M_2, \dots, M_5 : rear mirrors, G: grating of 100 grooves per mm, L_1, L_2 : KBr lenses, $f(L_1) = 10\text{ cm}$, $f(L_2) = 20\text{ cm}$)

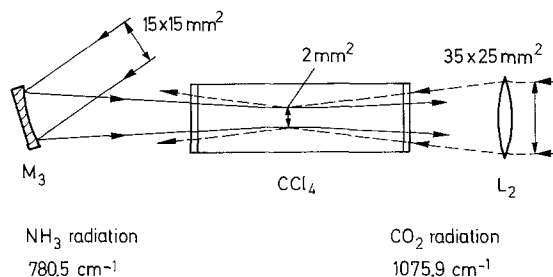


Fig. 2. Geometry of laser beams in two-frequency CCl_4 dissociation by NH_3 and CO_2 laser radiation

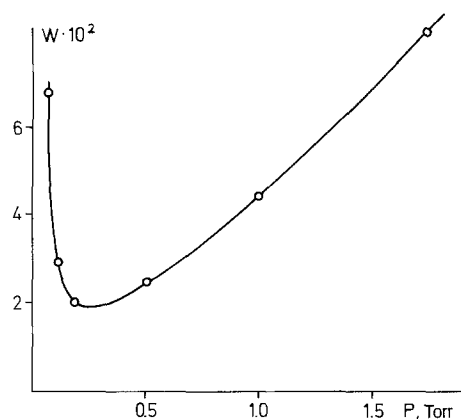


Fig. 3. Dependence of CCl_4 dissociation yield per pulse on initial pressure of CCl_4 . Focal energy density is $4.5 \text{ J} \cdot \text{cm}^{-2}$

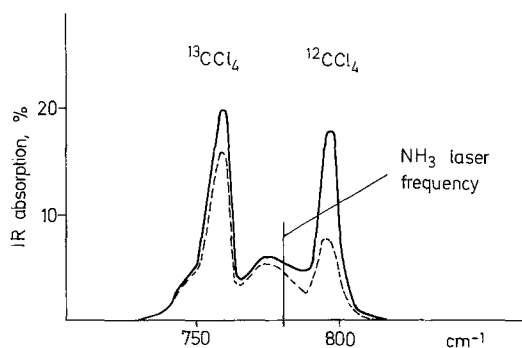


Fig. 4. Selective dissociation of ^{13}C enriched CCl_4 sample by NH_3 laser radiation. The solid line represents the IR absorption spectrum of CCl_4 before irradiation and the dotted line is the spectrum after irradiation. (Initial CCl_4 pressure was 0.25 Torr, focal energy density was $5 \text{ J} \cdot \text{cm}^{-2}$, and number of pulses was 1300)

Table 1. Effect of buffer gas on the CCl_4 dissociation yield and selectivity

Scavenger	Dissociation yield $W[^{12}\text{CCl}_4]$	Selectivity, $\frac{W[^{12}\text{CCl}_4]}{W[^{13}\text{CCl}_4]}$
—	0.046	2.8
O_2	0.055	1.95
C_2H_4	0.053	2.4

energy was 32–40 mJ, pulse length was 0.7–1.0 μs at the optimal NH_3 pressure (~ 4 Torr).

As shown in Fig. 1, this scheme is closed for CO_2 laser radiation. Together with the fast rotational relaxation in ammonia this greatly enhanced the pumping utilization. Secondly, the buffer gas (N_2 or air) was added to ammonia. This enhanced the output energy of the NH_3 laser up to 5 times at a buffer pressure of 15–20 Torr.

The spherical mirror M_3 and the lens L_1 focused the NH_3 laser radiation into the CCl_4 cell. Effective focal length of the $M_3 + L_1$ system measured from the lens was 6 cm that gave a focal energy density of 4–5 $\text{J} \cdot \text{cm}^{-2}$. In two-frequency experiments, a part of the CO_2 laser radiation reflected from the inclined NH_3 cell window was used. This radiation was directed and focused into the CCl_4 cell by flat mirrors M_4 and M_5 , and a lens L_2 . This reflected energy was 250–400 mJ, that gave an energy density in the focus of 12–20 $\text{J} \cdot \text{cm}^{-2}$. In a series of experiments, lens L_1 focusing NH_3 laser radiation was not used and the energy density in the CCl_4 cell decreased to 1.6 $\text{J} \cdot \text{cm}^{-2}$. The geometry of these experiments is shown in Fig. 2.

The CCl_4 cell made of stainless steel was 12 cm long and 1.2 cm i.d. and had KBr windows. A vacuum system with a residual pressure of 10^{-2} Torr was used for outgassing and filling. The CCl_4 samples of natural isotopic abundance and of ^{13}C enriched ($^{12}\text{C}:^{13}\text{C} = 38:62$) were used. The sample purity was 99%. Before filling, additional vacuum distillation was used.

The CCl_4 dissociation due to irradiation was characterized by a dissociation yield W which was determined as

$$W = \frac{1}{n} \ln \frac{N_0}{N},$$

where n is the number of pulses, N_0 the initial, and N the final molecule concentrations. The concentration ratio N_0/N was determined from the IR absorption spectrum of CCl_4 .

2. Single-frequency Experiments

2.1. Dissociation Yield

The NH_3 laser frequency (780.5 cm^{-1}) is close to the ν_3 mode frequency of $^{12}\text{CCl}_4$ (775 cm^{-1}). This mode is split into two absorption bands—one intense at 796 cm^{-1} and the second with broad maximum at 768 cm^{-1} . The laser frequency is between these two bands and the irreversible dissociation of CCl_4 takes place under irradiation.

The most interesting result is the dissociation yield as a function of the initial pressure of CCl_4 (Fig. 3). Unlike all the earlier known cases [1] this dependence has a

Table 2. Results of single- and two-frequency CCl₄ dissociation

Dissociation method	Energy density [J·cm ⁻²]		Dissociation yield $W[^{12}\text{CCl}_4]$	Selectivity, $\frac{W[^{12}\text{CCl}_4]}{W[^{13}\text{CCl}_4]}$
	$E(780.5\text{ cm}^{-1})$	$E(1076\text{ cm}^{-1})$		
Single-frequency	1.6	—	<0.001	—
Single-frequency	—	17	<0.001	—
Two-frequency	1.6	17	0.037 ± 0.003	1.85 ± 0.12

minimum at 0.25 Torr. The low-pressure part qualitatively agrees with analogous curve for SF₆ [6]. The most probable explanation of this part is that the multiple photon dissociation of CCl₄ has the unimolecular nature, as was shown for SF₆ [7], and that the collisions damp this process. At CCl₄ pressures higher than 0.25 Torr, the dissociation yield grows practically linearly with the pressure up to 2.0 Torr. This behavior may be attributed to thermal dissociation of CCl₄ after completion of $V-T$ relaxation in the focal volume.

The threshold energy density for the dissociation of CCl₄ is found between 1.6 and 2.0 J·cm⁻². Above the threshold the dissociation yield depends on the radiation intensity as $I^{4 \pm 1}$. If the focal energy density is 4.4 J·cm⁻², 3.4 parts in 10⁴ of CCl₄ molecules in the cell dissociate per one pulse at a initial pressure of 0.08 Torr. This corresponds to the dissociation yield of $W \sim 0.07$ for the molecules in the volume with the energy density higher than 1.6 J·cm⁻². At 6 J·cm⁻² (with an effective focal length of 4.5 cm) the W value reaches 0.1.

Addition of oxygen and ethylene to CCl₄ in the ratio CCl₄:O₂, C₂H₄ = 1 : 5 at a total pressure of 1.5 Torr did not increase considerably the dissociation yield with an energy density of 4 J·cm⁻², as shown in Table 1.

2.2 Isotopic Selectivity

In our experiments the isotopic selectivity for carbon isotopes was measured with the sample enriched with ¹³C isotope. This allowed to measure the selectivity by two independent ways: in the mass-spectrum of products formed as a result of dissociation (C₂Cl₄, C₂Cl₆) and on the IR spectrum of residual gas. In the first way, the selectivity was determined by the ratio of mass peaks ¹²C¹³CCl₃⁺, ¹³C₂Cl₃⁺, and ¹²C¹³CCl₄⁺, ¹³C₂Cl₄⁺, respectively; in the second way, by the ratio of dissociation yields for the two isotopes, as given by

$$s = \frac{W[^{12}\text{CCl}_4]}{W[^{13}\text{CCl}_4]}$$

Figure 4 shows an example of the isotopically selective CCl₄ dissociation. During irradiation of 0.25 Torr of the enriched CCl₄ by 1300 pulses of NH₃ laser radiation with 40 mJ per pulse in average ($\sim 5\text{ J}\cdot\text{cm}^{-2}$ in

the focal region) the selectivity was 4.4 ± 0.3 . The enrichment factor in the residual gas was 2.0 ± 0.1 , while the burnout gas was 40% (Table 2).

The simultaneous measurement of selectivity by two ways was carried out with an initial gas pressure of 0.3 Torr and total burnout of 8% of molecules. The dissociation yields gave a ratio of $s = 3.5 \pm 0.6$. The enrichment factor in newly formed products by ¹²C isotope was 4.5 ± 0.1 at peaks of C₂Cl₃⁺ and 6.2 ± 0.2 at peaks of C₂Cl₄⁺. Products enrichment with ³⁷Cl isotope has also been observed with enrichment factors of 1.12 ± 0.02 and 1.15 ± 0.02 , respectively.

Addition of scavengers O₂ and C₂H₄ in the same ratio 1 : 5 resulted in decrease of the enrichment factor (Table 1). Tentative explanation of this fact is that addition of scavengers shifts the ratio of molecules dissociated selectively in unimolecular fashion to those dissociated as a result of thermal processes (Fig. 3).

3. Two-Frequency Dissociation

The dissociation of CCl₄ by two laser pulses of different frequencies was also studied. In this method the whole process is divided into two stages: excitation and dissociation of excited molecules. The first stage is carried out by a comparatively weak resonant radiation, the second one by a nonresonant field of appropriate intensity [8]. In the case of an NH₃ laser it is convenient to use the CO₂ pump laser radiation at the second stage.

The geometry of the experiments is shown in Figs. 1 and 2. The main results are summarized in Table 2. With an energy density of 4.4 J·cm⁻² from the NH₃ laser in addition to the CO₂ laser, irradiating the same reaction volume in the CCl₄ cell, enhancement of the dissociation yield by a factor of 3 was achieved. The energy density from the CO₂ laser was 17 J·cm⁻² in the focal region.

Using the unfocused NH₃ laser radiation with an energy density of 1.6 J·cm⁻² and the CO₂ laser radiation (17 J·cm⁻²) a dissociation yield of $3.7 \cdot 10^{-2}$ per pulse was observed. In the case of either one laser the dissociation yield was below the detection limit if any. The isotopic selectivity in this case was 1.85 at a CCl₄ initial pressure of 0.25 Torr.

4. Discussion

The NH_3 laser is found to be very effective for the dissociation of CCl_4 . Ten percent of the molecules in the irradiated volume can be dissociated per pulse at a flux of $5 \text{ J} \cdot \text{cm}^{-2}$. This high efficiency from our point of view is connected with the shift of the NH_3 frequency against the peak absorption frequency of CCl_4 to the red. This type of enhancement of dissociation yield has already been observed in SF_6 dissociation experiments with the CO_2 laser [6]. High efficiency in both cases is connected with the fact that the laser frequency is close to the absorption resonance of high lying vibrational states of initially excited molecules. This absorption is known from the probing experiments to be shifted to the red from the linear absorption [9].

It is interesting to point out that the NH_3 laser radiation is 2–3 orders of magnitude more efficient for CCl_4 dissociation than the CO_2 laser radiation by action on the composite vibrational band $\nu_1 + \nu_2 + \nu_4$ [10]. Therefore, it is profitable to convert the CO_2 laser radiation into the NH_3 radiation and then to dissociate CCl_4 .

Behaviors of CCl_4 dissociation yield on the initial pressure, on the laser power, and on buffer gas all together indicate that the dissociation of CCl_4 goes in a unimolecular way. The enhancement of dissociation yield with the pressure is most probably connected with thermal dissociation of CCl_4 after full relaxation of the vibrational energy into the translational motion.

The results of two IR pulses do not allow unambiguous explanation. The main reason is that CCl_4 has a weak composite vibrational band at the frequency of the CO_2 pump laser. Therefore, if prepumped by the CO_2 laser, CCl_4 molecules are dissociated with the NH_3 laser

more effectively. This is the only reasonable explanation why the isotopic selectivity of dissociation drops in the case of two pulse experiments.

The observed high isotopic selectivity in dissociation products obtained even at non-optimal conditions (at a relatively high pressure) gives us hope that the CCl_4 molecule may be used as a starting material for carbon isotope production. This is also supported by the availability of NH_3 laser scaling. Of course, much work should be done to find the type of scavenger to be used in this method.

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