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Intensity and pressure effects in CO₂ laser induced carbon-13 enrichment with temporally modified pulses

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Abstract

Infrared multiple photon dissociation (IRMPD) of CF₂HCl has been studied under collisional conditions in the context of carbon-13 enrichment. Intensity and pressure effects have been investigated with temporally modified pulses generated from a TEA CO₂ laser using a simple, inexpensive plasma shutter device. Our results show that it is possible to achieve highly selective dissociation even upto a sample pressure of 250 Torr by 40 ns pulses under appropriate condition. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

In isotope selective photochemistry via infrared multiple photon dissociation (IRMPD), one is primarily concerned with the selective excitation of a desired species by a pulsed CO₂ laser and its subsequent reaction. The interplay dynamics between various energy transfer processes, $V-V'$, $V-R$, T , both intra and inter-molecular, which are in direct competition with radiative excitation limits the overall operating pressure for a desired selectivity [1,2].

Excitation by a conventional TEA CO₂ laser which has a temporal profile of about 100 ns spike and a few microseconds tail restricts the substrate pressure to typically less than a few Torr depending on various criteria like energy absorption by the system, laser intensity, spectral selectivity, etc. At higher pressure, serious selectivity loss occurs due to collisional processes which poses a major problem in a practical laser separation scheme where high pressure (> 100 Torr) operation is desired to reduce the reactor size and compressor cost. This may be tackled by employing a CO₂ laser delivering short pulses. In the past, there have been a few successful studies in this direction by using a modified temporal profile of a TEA CO₂ laser [3–5]. These short pulses can be obtained by various techniques like mode locking (both active and passive), free induction decay, pulse slicing with electro-optic switch [6–9]. However, output pulses from these

require further amplification for any useful application due to their very low energy content. One of the simplest and least expensive ways short pulses (a few tens of nanosecond duration) with appreciable energy output could be generated is by employing a 'plasma shutter cell' (PSC) [10–12]. Briefly, this involves laser induced dielectric breakdown of a gas kept in PSC. The gas which is normally insulating and transparent to the radiation at ordinary intensities is rapidly transformed into a highly conducting, self-luminous, hot plasma by the action of the high intensity laser pulse. The resultant plasma interacts with the excitation pulse and modifies its temporal profile. Though only a few IRMPD experiments were carried out using such an excitation source [10], we found this technique to be convenient for assessing the potential of short pulse irradiation for inducing isotopically selective dissociation at high pressures.

Freon-22, CF₂HCl, is an excellent system for practical separation of carbon isotopes [13–17]. Its well resolved carbon isotope shift facilitates highly selective photodissociation. It has a simple and facile laser chemistry. By virtue of its very low absorption cross-section at 1045 cm⁻¹, irradiation can be performed upto 100 Torr at a fluence ≤ 4 J cm⁻² by normal 100 ns pulses with a favourably low energy expenditure per separated carbon atom [13,15]. In the present study, the effects of shortened and temporally modified CO₂ laser pulses are investigated on the dependence of dissociation yield and selectivity with sample pressure. Our results show that highly selective dissociation is possible even upto 250 Torr with short pulses at appropriate conditions.

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2. Experimental

2.1. Short pulse generation by LIDB

A commercial TEA CO₂ laser (Lumonics 103-2) tuned to 9P (22) line (1045 cm⁻¹) was used in all the runs. The PSC (17 cm long and 5 cm diameter) made of brass and glass components was fitted with two plano-convex BaF₂ and ZnSe lenses (*f* = 10 and 7 cm, respectively). The laser beam was focused inside the tube by the first lens and rendered parallel again after passing through the second lens. High purity helium at various pressures was used in the plasma cell to generate short pulses. Suitability of He as a plasma medium was evaluated in terms of energy efficiency ($E_{\text{extracted}}/E_{\text{incident}}$) and duration of short pulses generated. Pulse energies were measured by a calibrated pyroelectric detector (GenTec-ED 500). A fast, room temperature, mercury-cadmium-telluride detector (Edinburgh Instruments, rise time < 1 ns) in combination with a 300 MHz digital scope (Lecroy 9450 A) was employed to capture the temporal profile. Pulse-to-pulse reproducibility of the plasma switch was found to be quite good (typically a few nanoseconds). Using different lasing gas mixtures with various amounts of N₂, we have further investigated how the temporal profile of incident pulse influences the generation and characteristics of the short output pulse.

2.2. Isotope selective photolysis by normal and short pulses

We have made a comparative photolysis study of CF₂HCl at various pressures using tail-free 100 ns FWHM pulses and also shorter pulses keeping irradiation conditions the same. For runs involving 100 nanosecond pulses, plasma cell was kept in evacuated condition while for shorter pulses it was filled with appropriate pressure of helium. Emergent beam from the cell was found to be well collimated and was focused into the centre of a pyrex photolysis cell (50 cm long, 3 cm diameter, overall volume 473 cc) by a BaF₂ lens. Commercial grade CF₂HCl (Mafron-22) was used as such after several freeze-pump-thaw cycles. Gas chromatography (Shimadzu RPR-G1) and mass spectrometry (VG Micromass 6060 F) were used to quantitatively measure the product formation and its carbon isotopes distribution [15–17]. Atom fraction ratio, (¹³C/¹²C) was measured for C₂F₄ by mass spectrometry from (*m/e*) peaks at 81 (⁺¹²CF₂¹²CF), 82 (⁺¹²CF₂¹³CF/⁺¹³CF₂¹²CF) and 83 (⁺¹³CF₂¹³CF), respectively with a precision of ± 1%. The combined analytical data yielded the decomposition yield for C-13 and C-12 bearing species, viz, ¹³Y and ¹²Y, respectively. The individual dissociation yield, ⁱY (*i* = 13 or 12) is given by:

$${}^iY = \{1 - ({}^iN_m / {}^iN_0)^{1/m}\} \times f \quad (1)$$

where ⁱN₀ and ⁱN_{*m*} correspond to the number of species containing the isotope '*i*' before and after irradiation with '*m*' number of pulses, respectively, '*f*' is the ratio between total reactor volume and irradiated volume. The dissociation selec-

tivity '*S*' is defined as the ratio of C-13 dissociation yield with respect to C-12 dissociation yield.

$$\text{i.e., } S = {}^{13}Y / {}^{12}Y \quad (2)$$

3. Results and discussion

3.1. Short pulse generation from PSC

Table 1 describes the results in terms of spike duration and energy efficiency for short pulses obtained from the plasma cell for different He pressures. Increase of gas pressure results in a gradual shortening of the transmitted pulse. However, the energy efficiency for the output beam gets progressively reduced.

In laser induced dielectric breakdown, the extremely rapid transformation from neutral gas into hot plasma takes place in three distinct phases, viz. (a) initiation, (b) formative growth and the onset of breakdown and (c) plasma formation accompanied by the generation of shocks and their propagation [11,12]. There are two mechanisms proposed for the initial ionisation. One involves ionisation by multiphoton absorption while the other involves cascade ionisation assisted by collisions. For excitation with an IR laser source, first process would involve simultaneous absorption of over hundred photons and is, therefore, less probable. As soon as conditions for the onset of breakdown are satisfied, ionisation growth will continue as long as the irradiation continues. There then follows the rapid plasma development stage and production of a highly ionised hot expanding gas in which further laser light absorption, heating and hydrodynamic processes become increasingly important. As the electron and ion concentrations increase, electron-ion and ion-ion interactions can contribute to the growth mechanisms. The gas will remain heated for substantially longer than the duration of laser pulse which created it, but the extinction processes of recombination, diffusion, radiation and conduction remove energy from the plasma region, and local thermodynamic equilibrium with surrounding gas is established in about microsecond time scale. Thus, laser induced dielectric breakdown acts like a switch allowing leading edge of the exciting laser pulse to pass through the plasma cell as a short duration

Table 1
Experimental conditions and results for short pulse generation in PSC^a

Gas	Pressure (Torr)	Spike duration (ns)	PSC Output energy (J)	% Efficiency ^b
He	0	100	0.64	100
	200	56	0.22	33
	250	40	0.29	35
	300	36	0.10	18

^a 100 ns FWHM pulses with very little tail were used for excitation.

^b Efficiency is defined as the ratio of output energy to incident energy of the beam entering the PSC after normalizing the window losses.

Table 2
Photolysis with pulses using variable nitrogen in the lasing gas mixture (LGM)

LGM ^a (l/min)	He pressure in PSC (Torr)	τ (Pulse) (Total) (μ s)	τ (Spike) (FWHM) (ns)	E (Total output) (J)	E (Spike) (J)	E (Tail) (J)	$^{13}\text{Y} \times 10^3$	$^{12}\text{Y} \times 10^6$	Selectivity S
0:1:8	0	2	100	0.64	0.58	0.06	14	930	15
0.1:1:8	0	3	100	0.65	0.34	0.31	3.9	650	6
0.2:1:8	0	4	100	1.11	0.33	0.78	44	18000	2.4
0:1:8	300	2	37	0.24	0.17	0.07	1.7	11	154
0.1:1:8	300	3	31	0.56	0.06	0.50	1.6	8	200
0.2:1:8	300	4	32	0.66	0.10	0.56	0.87	4.3	202
0.3:1:8	300	4	30	0.83	0.07	0.76	1.5	15	100
0.4:1:8	300	4	32	1.00	0.10	0.90	9.5	5000	1.9

^a LGM = N₂:CO₂:He. $\phi = 3.4$ – 5.6 J cm^{-2} in these runs.

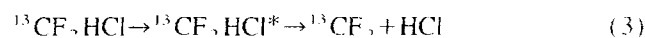
spike while absorbing/scattering the remaining part of the incident light.

With increase of gas pressure, threshold for breakdown goes on decreasing leading to an earlier onset of plasma formation. This results in a faster switching of the excitation pulse with a concomitant shortening of the transmitted pulse through the plasma cell. Energy efficiency for the output beam, however, gets progressively reduced because larger part of the excitation pulse gets absorbed/scattered.

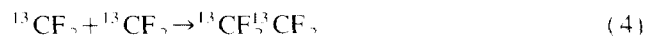
While trying to improve upon the energy of the short pulse with N₂ rich lasing gas mixtures delivering higher input energy, we found that tailing occurs in the extracted pulse. It appears, therefore, that under the present experimental conditions, residual part of the excitation pulse emerges as a tail after plasma extinction. This behaviour is more pronounced in the case of shorter ($\sim 30 \text{ ns}$) pulses which are generated at higher helium pressure in the plasma cell. In a separate study, we have investigated the temporal characteristics and partitioning of energy between the short spike and long tail of the output pulse (cf. Table 2). We have also used such modified pulses for isotope selective studies to see whether energy variation in the tail can help to improve IRMPD process.

3.2. Isotope selective photolysis by normal and short pulses

On selective excitation for the C-13 species, CF₃HCl undergoes facile dissociation:



where $^{13}\text{CF}_2\text{HCl}^*$ represents a highly vibrationally excited molecule. Dimerization of difluorocarbene results in the formation of tetrafluoroethylene enriched in C-13:



Depending on the excitation selectivity, collisional energy transfer, etc., some dissociation may occur for the C-12 species resulting in $^{12}\text{CF}_2$ formation. $^{12}\text{CF}_2$ thus formed can interact with either $^{13}\text{CF}_2$ or $^{12}\text{CF}_2$ producing different isotopic variants of C₂F₄. Ultimate isotopic composition of the

product depends on a number of parametric conditions prevailing during the photolysis which are discussed below.

3.2.1. Intensity effects

For a small molecule like CF₃HCl, laser intensity has a strong influence on its MPD [18,19]. Fig. 1 shows the dependence of ^{13}Y , ^{12}Y and S on incident energy for the photolysis of 100 Torr CF₃HCl by 100 ns pulses covering a fluence (ϕ) range upto 5.2 J cm^{-2} . While there is a steep dependence of Y in the threshold region ($\sim 2.5 \text{ J cm}^{-2}$), it is less pronounced for C-13 species above 3 J cm^{-2} . For C-12 species, however, the effect continues to dominate although at a diminished rate leading to a sharp decline in the selectivity. As the fluence is increased by a factor of three, S value drops from 170 to 3.

These results enable us to conclude that an increase in intensity causes a stronger excitation of the undesired isotope compared with the desired one giving rise to a lower dissociation selectivity. Several studies [20] on the spectra of multiphoton excited molecules show a broadening effect and diffusing of structure, if present, with increasing intensity. Therefore, irrespective of factors responsible for such changes like new multiphoton resonances, weak transitions, power broadening, etc., one can expect that an increase in

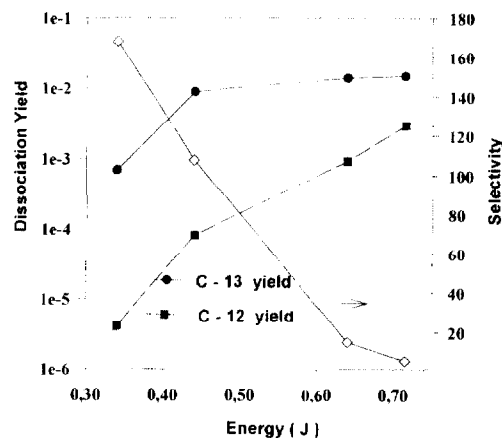


Fig. 1. Intensity dependence of runs with 100 ns pulses at 100 Torr CF₃HCl $\phi = 1.8, 3.2, 4.0$ and 5.2 J cm^{-2} .

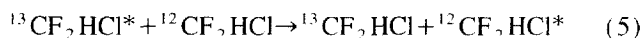
intensity, in general, brings down the selectivity. It is difficult, however, to carry out quantitative interpretation because our measurements have been taken at very high CF_2HCl pressure where inter isotopic $V-V$ exchange effects overwhelm purely field effects.

3.2.2. Pressure effects

Increase in gas pressure leads to rather a great number of collisions taking place during MPD. It has been observed that the processes of $V-V$, $V-T$ and rotational relaxation may have a pronounced and under certain conditions, a very significant effect on the MPD process and the observed yield for CF_2HCl dissociation [21,22]. In the case of excitation of a two component medium, collisional effects on selectivity are decided by different action of multicomponent collisional processes which could have many possibilities. The existence of several types of relaxation processes with varying rates causes the effect of collisions on selectivity to be highly dependent not only on the excitation conditions but also on the properties of the molecule being excited and the type of collision partner.

Here we present the essential results obtained in studying the influence of collisions on MPD selectivity. While describing these results, we will try to systematize them from the viewpoint of the contribution of different processes. A decrease in selectivity, S with increasing gas pressure is attributed to the process of $V-V$ exchange as a result of which transfer of vibrational energy to unexcited non-resonant isotopic molecule takes place during collisions. This causes the dissociation of these molecules to increase via two pathways: (a) the molecules with undesired isotope so excited are able to dissociate during the laser pulse and (b) post pulse dissociation through vibrational energy pooling. One more factor bringing down the S value is through the decrease in Y of the desired species as the pressure rises. This, for example, may take place when a considerable contribution to Y is made by the dissociation of C-13 molecules in relatively long lived states just above the dissociation limit. Such species are more vulnerable to collisional deactivation.

Effect of collisions on decomposition yields and selectivity were investigated at two different fluences in a pressure range of 50–150 Torr by 100 ns pulses. In this pressure regime, system undergoes several tens of collisions during the laser pulse which facilitate the $V-V$ exchange:



$^{12}\text{CF}_2\text{HCl}^*$ thus formed may end up in the vibrational quasi-continuum and undergo IR MPE/MPD leading to lowering of S . At a moderate fluence of 3.4 J cm^{-2} , both ^{13}Y and ^{12}Y continue to increase in a modest way upto about 100 Torr (cf. Fig. 2). However, selectivity is maximum at around 50–75 Torr in the range investigated and then begins to drop slowly which could be due to the difference in rate of rotational relaxation for the two isotopic molecules. But beyond 100 Torr, the accelerated $V-V$ deactivation of C-13 species with consequent increase in ^{12}Y leads to a sudden drop in selectivity which is about 20 at 150 Torr. The general trend

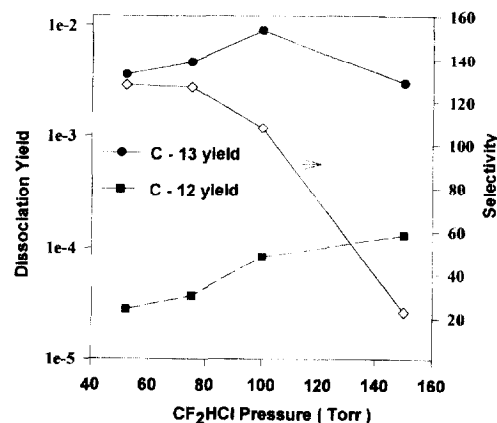


Fig. 2. Pressure dependence for photolysis with 100 ns pulses $\phi = 3.4 \text{ J cm}^{-2}$.

of our results for photolysis of 50–150 Torr CF_2HCl by normal pulses of 9 P(22) line at 3.4 J cm^{-2} is similar to that reported for a pressure range of 10–200 Torr by 9 P(20) irradiation at 3.2 J cm^{-2} in Ref. [13] and for a range of 7.5–75 Torr by 9 P(26) at 4 J cm^{-2} fluence in Ref. [22]. We have further found that increasing the fluence to 5.2 J cm^{-2} resulted in an enhanced dissociation of C-12 species even at an early stage of about 50 Torr. Moreover, selectivity values which were much lower than those at moderate fluence irradiation at a given pressure dropped to a very low value of about 2 at 150 Torr. Our main aim in this study is to overcome selectivity constraints in normal pulse excitation. This has been achieved (vide infra) by employing temporally modified short pulses for irradiation at high sample pressures. For example, we have shown that a high selectivity of 70 can be preserved even at 250 Torr for photolysis with 40 ns pulses.

3.2.3. Pulse duration effect

A fairly reasonable modelling [23] has been done to correlate the selectivity with $V-V$ exchange rate constant, k_{V-V} , total gas pressure, p and laser pulse duration, τ_p . It follows from the model that in exciting a minor isotopic component (fractional abundance, $x_0 \ll 1$), it is possible to work with a high gas pressure if the spectral dissociation selectivity S_0 is large enough to be $> 1/x_0$. In this case, the enrichment depends on the partial pressure, p_0 of the desired isotope ($p_0 = px_0$) and so the operating gas pressure could be sufficiently high. For CF_2HCl photolysis, with right choice of excitation frequency, temperature, etc., above condition can be fulfilled and a dissociation selectivity of 90 could be maintained even at 100 Torr total pressure of CF_2HCl [13–15]. By fitting experimental results on various systems to this model, it has been possible to arrive at a general condition: $p_0 S_0 k_{V-V} \tau_p = \text{constant}$, for optimising various experimental parameters. Therefore, by changing τ_p , we can affect the contribution of $V-V$ exchange on the measured value of selectivity and hence vary the dependence of S on pressure.

For photolysis runs in this category, pulses of different durations (100–30 ns) were generated by adjusting helium pressure in the plasma cell. CF_2HCl pressure was kept at 100

Table 3
Photolysis with pulses of variable spike duration ^a

He pressure in PSC (Torr)	τ (Pulse) (Total) (μ s)	τ (Spike) (FWHM) (ns)	E (Total output) (J)	E (Spike) (J)	E (Tail) (J)	$^{13}\text{Y} \times 10^3$	$^{12}\text{Y} \times 10^6$	Selectivity (S)
0	3	100	0.65	0.34	0.31	3.9	650	6
100	3	83	0.48	0.18	0.30	1.87	12	156
150	3	50	0.34	0.10	0.24	1.16	7.6	153
200	3	36.5	0.53	0.13	0.40	1.04	9.3	112
300	3	31	0.56	0.06	0.50	1.60	8.0	200

^a 100 Torr CF_2HCl was photolysed at 4 J cm^{-2} fluence in all the runs. LGM:0.1:1:8 l/min.

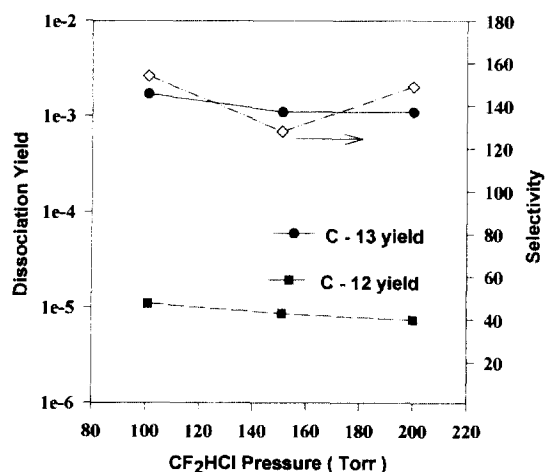


Fig. 3. Pressure dependence for photolysis with 40 ns pulses $\phi = 3.7 \text{ J cm}^{-2}$.

Torr and average focal fluence was 4.0 J cm^{-2} in all these runs. The results are given in Table 3. By decreasing the pulse duration by a factor of three down to 30 ns, we could further improve upon the selectivity to 200 at 100 Torr sample pressure. An estimate of k_{v-v} from these measurements was found to be $10^6 \text{ Torr}^{-1} \text{ s}^{-1}$ which is typically the value for such a small molecule.

Similar information was obtained by working with a shortened pulse on higher sample pressure while retaining the dissociation selectivity at a fairly high level. Fig. 3 shows the dependence of ^{13}Y , ^{12}Y and S on system pressure while working with 40 ns pulses. At a fluence of 3.7 J cm^{-2} , collisions play only a marginal role on the decomposition yield of either of the isotopic species in the pressure range investigated. A high dissociation selectivity of about 150 is maintained throughout compared with those from photolysis by 100 ns pulses (cf. Fig. 3). When the focal fluence was raised to 4.5 J cm^{-2} , S was found to be ~ 40 at 50/75 Torr, and ~ 70 for a substrate pressure range of 100–250 Torr. At 300 Torr, it dropped to 8.

Investigation of the influence of N_2 in lasing gas mixture on both temporal profile and energy partitioning between the spike and tail components was done under two conditions, viz., (i) evacuated plasma cell and (ii) with 300 Torr He (cf. Section 3.1). Such temporally modified pulses with varying tail energy content were employed in the photolysis of

100 Torr sample. The motivation of applying such temporally long pulse was to see any modification of yield/selectivity of the process. We have seen that increasing pulse energy in the microsecond tail part of a 100 ns FWHM pulse resulted in a drastic fall of selectivity. However, when 30 ns FWHM pulses in conjunction with varying tail energy were employed, selectivity could be maintained at a similar level (~ 100 – 200) (cf. Table 2) as obtained with the short spike only. This can be understood by considering CF_2HCl as a small sized molecule having a high lying quasi-continuum onset which also suffers from molecular sticking [24] in the last stages of discrete vibrational ladder. Therefore, supply of extra energy in the form of tail merely populates the vibrational levels of discrete ladder without causing any noticeable enhancement in dissociation yield and hence the selectivity. On the contrary, quantum efficiency of MPD in such cases are observed to be lower compared with that obtainable using tail-free pulses.

4. Conclusion

We have standardised a technique based on laser induced dielectric breakdown in He to generate TEA CO_2 laser pulses of short duration with good reliability and useful energy output. These pulses have been successfully employed for carbon-13 enrichment in the photolysis of neat CF_2HCl at pressures as high as 250 Torr. Optimisation of these results are expected to be very useful in the scaling up of C-13 enrichment by laser separation method.

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