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Efficient Production of $^{13}C_2F_4$ in the Infrared Laser Photolysis of $CHClF_2$*

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Abstract. We report the isotopically selective decomposition of chlorodifluoromethane. Chlorodifluoromethane is used industrially in high volume for the production of tetrafluoroethylene and its polymers; thereby it is an attractive working substrate for a medium scale isotope separation process, both in terms of its price and availability.

We have studied the infrared multiphoton decomposition of carbon-13 substituted chlorodifluoromethane molecules present at their natural abundance (1.11%). A well defined CO_2 laser pulse (80 ns FWHM) was used and both the yield of carbon-13 enriched product and the net absorption of laser radiation were measured. These measurements were made as a function of substrate pressure (10–800 Torr), CO_2 laser line (9P12–9P32) and fluence (2–8 J cm^{-2}) and were used to determine the energy expenditure per carbon atom produced (ε) at specified product carbon-13 content in the range 30%–96%. The results of these parametric studies were interpreted in terms of the kinetics of multiphoton absorption and dissociation, and allowed an initial optimization of the experimental conditions to minimize ε.

Optimum results were obtained at 1046.9 cm^{-1}, 69 cm^{-1} to the red of the $^{12}CHClF_2$ ν_9 band center. Irradiation of 100 Torr of chlorodifluoromethane at 3.5 J cm^{-2} gave tetrafluoroethylene containing 50% carbon-13 for an absorption of 140 photons (0.017 keV) per carbon atom produced. This efficiency compares favourably with existing carbon-13 enrichment technologies and would require an absorption pathlength of only 2 m to absorb half the incident photons.

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Since the suggestion first appeared that the absorption of laser radiation and subsequent decomposition of molecules could be isotopically selective, a good deal of work has been done to demonstrate enrichment for a number of isotopes using various lasers covering the spectral range from the vacuum ultraviolet to the far infrared. Very highly selective decomposition of hydrogen isotopes has been demonstrated using infrared lasers as the molecular isotope shift is large. Results on isotopes of sulfar and boron have shown the method to be promising and probably generally applicable to any element even the heavy ones including uranium. It is not the purpose of this introductory section to provide a comprehensive review of work done, instead literature will be used to exemplify the important points necessary to the design of an efficient infrared-laser-based photochemical isotope separation process. Important factors in optimizing such a process include: the spectroscopy, optical selectivity and detailed photochemistry of the chosen substrate, and the frequency, fluence and pulse shape of the laser. These in turn define the overall selectivity factor, the working pressure and temperature, and photon utilization factors for possible configurational optimization in defining an engineered system.

The linear, low-intensity optical selectivity is important only in so far as it indicates the potential for selective infrared multiphoton decomposition. Marling

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and co-workers have demonstrated very high optical selectivities for D/H systems and report selectivity factors in the range of 10^4 for the multiphoton decomposition (MPD) of natural isotopic abundance trifluoromethane at 100 Torr pressure by CO_2 laser pulses of 2 ns duration [1]. For heavier atoms the vibrational isotope shifts are less and the detailed spectroscopy becomes increasingly important. For example, we have compared the MPD of the series CF_3X, X: Cl, Br, I, and showed that the presence of a combination band limits the $^{13}C/^{12}C$ selectivity factors obtainable from CF_3I [2]. On the other hand, isolated narrow bands such as in perfluoropropene [3] and hexafluoroacetone [4] give a narrow spectral dependence of dissociation and high selectivities for isotopic substitution at the (vibrationally) active site of the molecule, with selectivity factors for the decomposition of natural abundance mixtures of $CF_3{}^{13}COCF_3$ and $CF_3{}^{12}COCF_3$ approaching 10^3.

The ensuant photochemical mechanism which relates stable products to the primary fragments is also of major importance in that the photophysical selectivity must be carried over to stable products to as great an extent as is possible. Thus any fragment-substrate reactions which scramble or degrade the primary selectivity are undesirable, as are back reactions which reduce the primary yield. The MPD of hexafluoroacetone in the ν_{15} band produces carbon monoxide which carries all of the isotopic selectivity. This product is easily separable and inert thereby retaining both the primary yield and selectivity. In other systems, for example the CF_3X molecules, very significant loss of primary yield occurs because of radical-atom recombination while in others, the intrinsic selectivity is degraded either because of reaction sequences or because the photo-products absorb at the same wavelength as the primary substrate and therefore undergo secondary photolysis reducing the yield and dispersing the selectivity over a complex array of final product [2].

The requirements that a laser provide the proper frequency is clear. The intention is to selectively excite one isotopic variant leaving others unexcited. It is probably worth emphasizing in passing the importance of pulsed CO_2 lasers. Many molecules have absorption features in the 1000 cm^{-1} region and the CO_2 laser is by far the most cost effective device commercially used in terms of unit costs per watt of output optical power [5]. However, given the availability of an efficient laser at the appropriate frequency, other requirements must be met if high selectivity and yield are to be achieved. The spectral requirements for each *stage* of the primary excitation have been demonstrated in a study on the two laser decomposition of hexafluoroacetone. The intention in these experiments was to demonstrate differing requirements for driving the molecules through the difficult, rate determining Region I, to those required to drive the excited molecules through Region II to dissociation [4, 6]. Given a narrow linear absorption band, the spectral dependence of the Region I excitation is narrow while that of Region II excitation is broad. This fact limits the pressure regime for selective dissociation of the major isotopic component as collisional processes may lead to the minor component reaching Region II and then being pumped to dissociation. If the minor component is selectively excited, or if the major component is excited far from resonance such that only a small fraction of initial states communicate with the field, then the residue represents a significant cold bath which quenches collisional contributions to the up-pumping.

The effect of the temporal intensity profile of the laser pulse is more difficult to define. For a given pulse shape, the fluence or energy per unit cross sectional area of the beam was shown to govern the rates of multiphoton absorption in the quasicontinuum Region II [6, 7]. However intensity effects must clearly be important in both driving the molecules through the rate determining Region I and in affecting the lifetime of the dissociating species in Region III by controlling the degree of excitation above threshold. Even for a fixed profile, the optimum fluence for selectivity seems ambiguous, in some cases high selectivities were obtained at threshold fluence [8] whereas in other systems, for example chlorotrifluoromethane, selectivity factors were independant of fluence over a considerable range [9].

Almost all infrared multiple-photon dissociation studies involve sub-atmospheric pressures although there is a clear engineering preference for a high working pressure. This reduces the absorption path length, pumping requirements and makes the whole concept of mass transfer easier. The optimum pressure for selective dissociation is dependent upon the relationship of the laser frequency with respect to the absorption (i.e. the number of initial states that communicate with the laser field) and the laser pulse width. The main factors limiting pressure are: (i) rotational relaxation which increases the number of states that interact with the laser pulse; (ii) collisional processes in Region I which decrease the rate of passage through the rate determining step(s), although this can give very significantly higher selectivities [3, 8, 10] when a minor component is excited, these are only achieved by losses in the decomposition yield as a whole and decrease the efficiency of photon utilization; (iii) collisional processes in Region II which deactivate molecules with energies close to the decomposition threshold thereby reducing the yield; (iv) collisional energy transfer thereby reducing the selectivity by introducing a significant contribution from non-selective thermal decomposition [11, 12] resulting from collisional "leakage" through the rate determining region. Taken together, these suggest the need for a relatively short pulse duration of the order of 10–100 ns if efficient, selective multiphoton dissociation is required at pressures in the region of 100 Torr. This argues against the use of nitrogen in the gas mix of TEA CO_2 lasers as this leads to a tail of some microseconds duration [13].

In commercial terms the factor which must be optimized is simply the cost per unit production for material at a given degree of enrichment. The nearest equivalent we have in the present context is the photon utilization efficiency, or put differently, the energy which must be absorbed to produce one separated atom at the given degree of enrichment. Unlike uv processes where the "quality" of photons differ in terms of bandwidth and absolute wavelength leading to very different values, infrared photons for MPD are much more homogeneous in value since wavelength and bandwidth considerations are not highly critical and overall laser efficiencies for even relatively short pulses (~ 50 ns) are not markedly lower than "normal" values.

As we shall see, chlorodifluoromethane MPD rates well against each of the parameters and given its relatively low bulk price must be considered a serious contender in any proposed ^{13}C separation scheme.

In the 9–11 µm region, the infrared absorption of matrix isolated chlorodifluoromethane consists of two $C-F_2$ stretching fundamentals, the ν_9 antisymmetric A'' at 1116 cm^{-1} and the ν_3 symmetric A' at 1099 cm^{-1} [14]. These bands are unresolved in room temperature gas phase spectra. At $-70°$ C a side band appears at 1083 cm^{-1} which we assign to a $C-F_2$ stretching vibration of $^{13}CHClF_2$, shifted by 33 cm^{-1} to the red of the ν_9 band of $^{12}CHClF_2$ [15].

This shift is in reasonable agreement with the shifts observed in the two $C-F_2$ stretching modes of the $Cl-H-(CF_2)^-$ anion where the 1143 and 1253 cm^{-1} bands shift to 1117 and 1223 cm^{-1} on ^{13}C substitution [16].

The decomposition of $CHClF_2$ takes place via a single product channel to give HCl and CF_2 in both thermal decomposition and MPD [17–20]. Using a molecular beam setup and measuring both angular and time-of-flight distributions of the fragments from the MPD of $CHClF_2$ excited at 1082.3 cm^{-1} it has been shown that the main decomposition channel is HCl elimination as it is for the pyrolytic unimolecular reaction [17]. The laser induced decomposition of $CHClF_2$ has also been studied under collisional conditions with time resolved probing of the dominant reaction products by optical absorption and infrared emission spectroscopy [21] with the emphasis being placed on IRMPD under collisional conditions where energy pooling between $CHClF_2$ molecules can be a dominant route to dissociation. Further studies monitored the appearance of the CF_2 product in real time during and after the laser pulse [18]. The difluorocarbene radicals were detected quantitatively by their optical absorption in the $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ band system around 250 nm.

This paper reports a parametric study of the ^{13}C selective infrared MPD of chlorodifluoromethane using a well defined tail-free CO_2 laser pulse of 80 ns FWHM. Yields of products and infrared energy absorbed were measured in each experiment for the same condition.

Experimental

For most of this work, a 10 cm long, 136 cm^3 volume, pyrex cell equipped with NaCl windows was connected to the inlet of a Finnigan 1020 GC/MS through a low pressure sampling valve. Chlorodifluoromethane (Matheson) at pressures of 10–800 Torr was irradiated with 1–1000 pulses of the collimated beam of a Lumonics 103 TEA CO_2 laser using a N_2 free mixture to reduce the tail. The initial spike was 72 ns FWHM and the time to transmit 30%, 50%, and 90% of the pulse energy was 75 ns, 100 ns, and 1.0 µs, respectively [13]. The laser beam passed through an 18 mm diameter aperture and was then collimated into the cell by a 100 cm focal length germanium lens positioned 100 cm from the center of the cell and finally apertured to 3 mm diameter in front of the cell. In all experiments the yields and absorbed energy were measured together. In situations where the absorbed energy was too small to be measured accurately it was extrapolated from absorption measurements at higher pressures and/or in a longer cell. The incident energy was monitored by a pyroelectric detector which viewed the reflected light from a NaCl beam splitter positioned in front of the 100 cm lens. This detector was calibrated with a Scientech Model 360001 disk calorimeter measuring the energy of a suitably attenuated beam. The transmitted intensity was measured by a second (calibrated) pyroelectric detector viewing the transmission through two germanium attenuators placed behind the cell.

Very small amounts of impurities CF_4, CO_2, CF_3H and C_2F_4 in the Matheson 99.9% chlorodifluoromethane were completely removed by first passing the gas over NaOH to remove CO_2 then by as many freeze-pump-thaw cycles in *n*-pentane slush at $-120°$ C as needed to reduce the others below the GC/MS detection limit. The conversion was always low and the amount of C_2F_4 produced varied linearly with the number of pulses in the range 1–400 pulses.

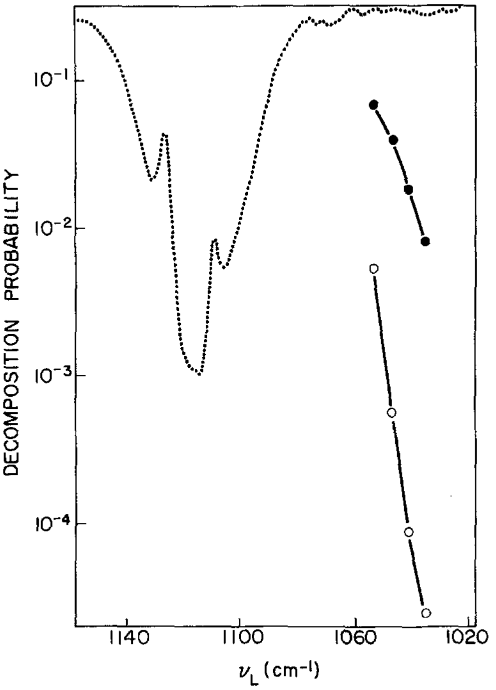

Fig. 1. Decomposition probabilities of ^{13}C bearing molecules ● and ^{12}C bearing molecules ○ as a function of laser frequency ν_L for 100 Torr of chlorodifluoromethane and 4.0 J cm^{-2} fluence in the frequency region of high ^{13}C selectivity. Laser lines used were 9P12, 9P20, 9P26, and 9P32 at 1053.9 cm^{-1}, 1046.9 cm^{-1}, 1041.3 cm^{-1}, and 1035.5 cm^{-1} respectively. The ν_9 band contour, 1.0 Torr pressure, 18 cm path length, is shown for reference

After irradiation, samples were subjected to thermal cycling to ensure uniform mixing. Calibration of the GC/MS response was achieved with aliquots of C_2F_4 corresponding to the amounts produced in experiments and diluted with the same total pressure of substrate used in the irradiations. Mixtures (either from irradiated samples or premixed calibration samples) were simply expanded into a previously evacuated sampling loop than injected with helium as the carrier gas at 20 ml min^{-1}. A 75 cm long, 3 mm OD, stainless steel column packed with 80–100 mesh silica gel used isothermally at 120° C gave retention times of 55 s and 115 s for C_2F_4 and $CHClF_2$ respectively. Other potential products such as CF_2Cl_2, C_2F_5H, $C_2Cl_2F_4$, C_2F_4HCl, C_3F_6, and C_3F_8 were carefully sought in high conversion runs using a column of 180 cm Chromosorb 102 + 180 cm silica gel but the only product observed was C_2F_4. Aliquots of CF_3H and C_2F_6 were injected to obtain upper limits for their production and it was shown that these were produced in amounts smaller than 0.1% of C_2F_4. Finally, the different isotopic combination peaks for the $C_2F_3^+$ ions at m/e 81, 82, 83 showed a simple binomial distribution ($a^2:2ab:b^2$) confirming that CF_2 radical combination was the sole product source and that this source was homogeneous. Any departure from statistical distribution at irradiation frequencies close to band center are accounted for in the discussion. The measured yields were reproducible well within ±5%.

Results

The intrinsic ^{13}C selectivity factor, α, obtains from the following relationship:

$$\alpha = \ln(1 - {}^{13}f)/\ln(1 - {}^{12}f), \qquad (1)$$

where ^{13}f and ^{12}f are respectively the fractional decomposition of $^{13}CHClF_2$ and $^{12}CHClF_2$ which in turn are calculated from the amount of tetrafluoroethylene produced and its ^{13}C atom fraction x'. The decomposition probability of irradiated $^{12}CHClF_2$ molecules, $^{12}P_d$, is given by

$$^{12}P_d = \frac{^{12}\text{C bearing molecules decomposed/pulse}}{^{12}\text{C bearing molecules irradiated/pulse}}. \qquad (2)$$

For most of the experiments reported here, $^{12}P_d$ was less than 3×10^{-3} and therefore within the precision of the present data was equal to its initial or intrinsic value. The initial or intrinsic value of the $^{13}CHClF_2$ decomposition probability $^{13}P_d$ is then given by

$$^{13}P_d = \alpha\,{}^{12}P_d. \qquad (3)$$

The values of $^{13}P_d$ and $^{12}P_d$ for 100 Torr $CHClF_2$, 4.0 J cm^{-2} fluence, and obtained at various irradiation frequencies are shown in Fig. 1. At 50 Torr pressure and for three irradiation frequencies, the probabilities increase with fluence as is shown in Fig. 2. Figure 3 details the effect of pressure on the dissociation probability for the same three irradiation frequencies at constant fluence (3.2 J cm^{-2}). The fractional absorption is almost independent of fluence and linear in pressure as is detailed in Figs. 4–6 for three different excitation frequencies. Data of this type allow the determination of ε (in units of keV/C-atom)

$$\varepsilon = 6.2 \times 10^{15}\, E_{\text{abs}}/N, \qquad (4)$$

where E_{abs}: absorbed energy [J]; N: number of carbon atoms produced per pulse.

Discussion

The data presented in Figs. 1–6 are entirely typical of results obtained from studies of selective infrared multiphoton dissociation of carbon-13 substituted molecules, as discussed in the introduction. The results presented in Fig. 1 demonstrate the interaction be-

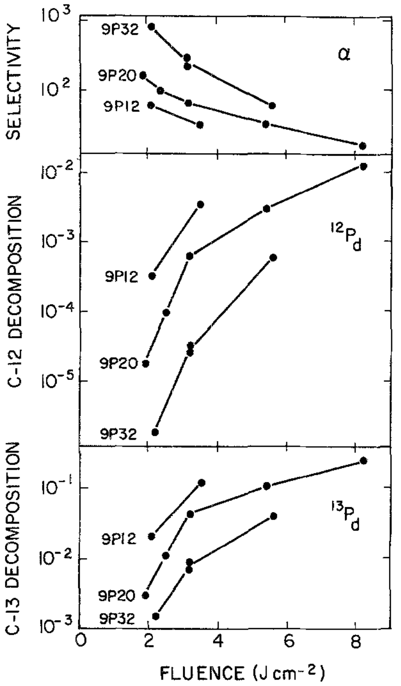

Fig. 2. Decomposition probabilities of ^{12}C and ^{13}C bearing molecules as a function of incident fluence for 50 Torr of chlorodifluoromethane and three different irradiation frequencies

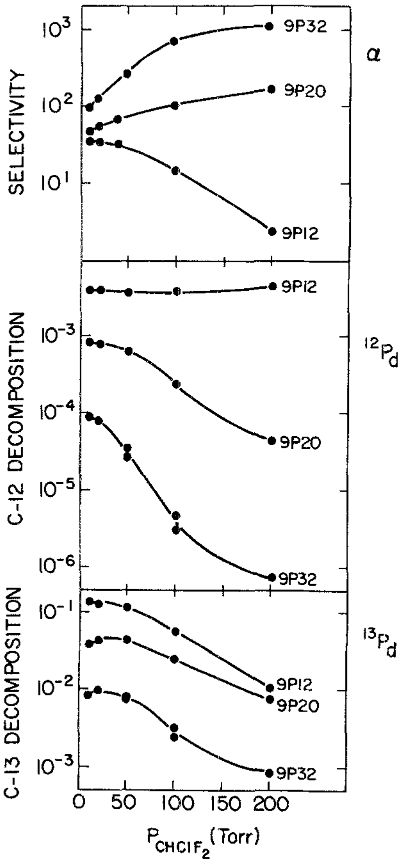

Fig. 3. Decomposition probabilities of ^{12}C and ^{13}C bearing molecules as a function of pressure of chlorodifluoromethane at 3.2 J cm^{-2} incident fluence for three different irradiation frequencies

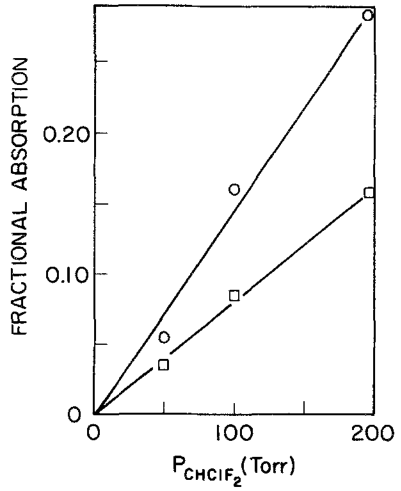

Fig. 4. Fractional absorption of 1053.9 cm^{-1}, 9P12, laser radiation through 10 cm path length of chlorodifluoromethane as a function of pressure for two different fluences: ○ 3.5 J cm^{-2}; □ 2.1 J cm^{-2}. Enhanced absorption at higher fluence indicates thermal heating of the bulk gas, resulting in pyrolysis as discussed in text

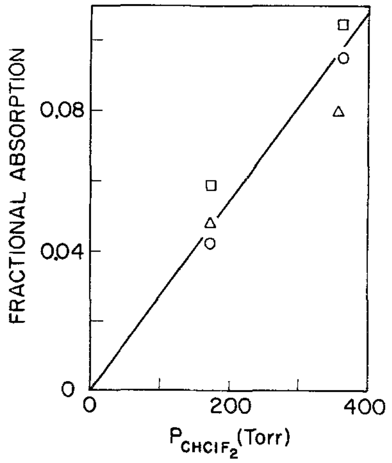

Fig. 5. Fractional absorption of 1046.9 cm^{-1}, 9P20, laser radiation through 10 cm path length of chlorodifluoromethane as a function of pressure for three different fluences: ○ 3.4 J cm^{-2}; □ 2.4 J cm^{-2}; △ 1.9 J cm^{-2}. Absorption is independent of fluence

tween the pumping rate and vibrational quenching rate through Region 1 determining the isotopic selectivity. This interaction may be more clearly demonstrated by the data in Fig. 3 which shows the effect of pressure in the range 10–200 Torr for irradiation at 1053.9 cm^{-1}, 1046.9 cm^{-1}, and 1035.5 cm^{-1}, the 9P12, 9P20, and 9P32 CO_2 laser lines, respectively. An interesting feature of these data is the converging selectivity at vanishing pressures for the three irradiation frequencies used. This was predicted from the decomposition of CF_3COCF_3 [4] where the shape of the decomposition spectra of the two isotopic variants separated by the isotopic shift readily divided the

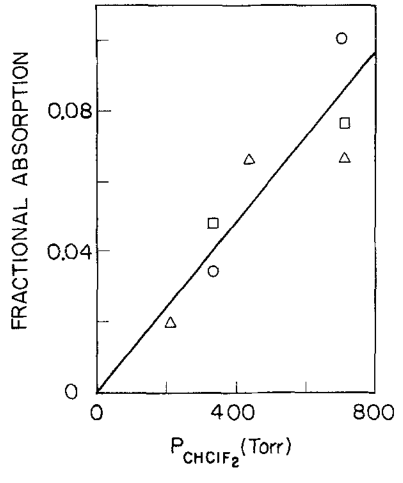

Fig. 6. Fractional absorption of 1035.5 cm^{-1}, 9P32, laser radiation through 10 cm path length of chlorodifluoromethane as a function of pressure for three different fluences: ○ 3.2 J cm^{-2}; □ 2.5 J cm^{-2}; △ 2.2 J cm^{-2}. Absorption is again independent of fluence. Within the accuracy of our measurements, Figs. 3–5 indicate that fractional absorption increases linearly with pressure

frequency scale into three regions, one on the blue side of the $CF_3{}^{12}COCF_3$ decomposition maximum, one between the two maxima and the third on the red side of the $CF_3{}^{13}COCF_3$ maximum. In the first and third regions, the selectivities should be independent of frequency at low pressures. This independence was also observed for low pressure selective decomposition of mixtures of dichlorodifluoromethane and oxygen [22]. We are presently studying a series of molecules under these conditions where the actual decomposition probabilities will give some insight into the multiphoton excitation which in turn depends on absorption band intensity, bandwidth, spectroscopy, molecule size, etc.

The probabilities decrease with pressure, as observed in CF_3COCF_3 [4] and CF_3Br [10], at the three irradiation frequencies in the high-pressure range and the selectivity factors increase with pressure. For both ^{13}C and ^{12}C bearing molecules, collisions within the cold bath of ^{12}C unexcited molecules relax the molecules in Region I of multiphoton excitation, in competition with up-pumping by the laser field. The up-pumping rate depends upon the off-resonance energy and hence it is not unreasonable that carbon-13 isotopic selectivities generally increase with increasing pressure and decrease with increasing frequency in this kinetic situation.

Conversely, closer to the band, at 9P12 irradiation frequency, increasing the pressure increases $^{12}P_d$ and decreases α due to pyrolysis. An analogous result to that observed in earlier studies on CF_3Br [11]. In the present case as well, the statistics of the isotope peaks in the mass spectra of the product C_2F_4 revealed two different product sources at different enrichments, for extreme cases of low irradiation frequencies, high fluences and high pressures.

The data presented in Fig. 2 are entirely consistent with other IRMPD dissociation studies. The reaction probabilities increase as a strong function of fluence. Obviously, with increased fluence there is an absolute limit of one to probabilities so $^{13}P_d$ tends to level off sooner at high fluences and the selectivity factors decrease with fluence. Since the fractional absorption is almost independent of fluence (Figs. 4–6), the amount of energy absorbed per carbon atom produced (ε) decreases drastically with increasing fluence ranging for the example of 9P32 irradiation, from 0.26 keV/atom down to 0.019 keV/atom when fluence is varied from 2.2 to 5.6 J cm^{-2}.

The most efficient set of conditions for selective decomposition of $^{13}CHClF_2$ at natural abundance can now be easily specified from Figs. 2 and 3 and from the additional data where fluence was varied at other pressures and pressure varied at other fluences as summarized in Table 1 which contains the parameters frequency, pressure and fluence for the least energy

Table 1. Energy expenditures ε at the optimum conditions of laser frequency[a] ν_L, working pressure P and fluence F for the single step ^{13}C selective decomposition of chlorodifluoromethane as a function of C_2F_4 product ^{13}C atom fraction x'

x'	ν_L [cm^{-1}]	P [Torr]	F [J cm^{-2}]	$^{13}P_d$	ε [keV/C-atom]	L_c^{50} [m]
0.3	1046.9	50	5.4	1.1×10^{-1}	0.009	3.8
0.4	1046.9	50	3.2	4.4×10^{-2}	0.013	3.8
0.5	1046.9	100	3.5	4.0×10^{-2}	0.017	1.9
0.6	1035.5	50	4.2	2.4×10^{-2}	0.043	8.3
0.7	1035.5	50	3.2	7.7×10^{-3}	0.062	8.3
0.8	1035.5	75	3.2	5.0×10^{-3}	0.145	5.6
0.9	1035.5	100	3.2	2.3×10^{-3}	0.260	4.1
0.96	1035.5	200	3.2	9.0×10^{-4}	0.760	2.0

[a] CO_2 laser lines 9P20 and 9P32 at 1046.9 cm^{-1} and 1035.5 cm^{-1}, respectively

Table 2. Separation energies for ^{13}C at 95+ % enrichment[a]

Process	Substrate	α[b]	Separation[c] energy [keV/C-atom]
Thermal diffusion[d]	CH_4	6.2	[d]
Gaseous diffusion[e]	CH_4	1.02	[e]
Distillation[f]	CO	1.0076	1.5
Chemical exchange[g]	$CO_2/R_2NCO_2^-$	1.010	9.1
uv laser chemistry[h]	H_2CO	30	14.8
ir laser chemistry[i]	CF_3Br	38	1.5
ir laser chemistry[j]	CF_3COCF_3	90	2.8
ir laser chemistry[k]	$CHClF_2$	90	1.0
ir laser chemistry[l]	$CHClF_2$	38	0.8

[a] Independent of production rates

[b] Stage separation factor; first stage for laser-chemistry processes

[c] Assuming the following for laser-chemistry processes: 1) Yields and selectivity factors are the same in each stage that is independent of atom fractions in starting material, 2) neglecting the energy to convert first stage product to a separable substrate, 3) this is a batch process where the tails in the first stage are discarded and the second stage recovers all the ^{13}C, and 4) the process separation energy is the first stage energy times $(1+1/x')$ where x' is the first stage product atom fraction

[d] Equilibrium separation factor given for a column 7.5 cm long, inner wall 3.5 cm dia. at 300 °C, outer wall 5 cm dia. at 15 °C and 400 Torr CH_4 pressure [24]. Process featuring lowest production cost for low production rates <200 g/a ^{13}C [25]

[e] Energy requirements are large but much smaller than for thermal diffusion [25]

[f] Process with lowest production costs at large production rates [26]. This separation energy is from Stachewski's [26] 20 kWh/mole doubled to account for low efficiency of liquid nitrogen heat transfer

[g] From Stachewski's [26] 251 kWh/mole

[h] ^{22}Ne II ion laser selective decomposition of $H_2{}^{13}CO$ at natural abundance at 332.271 nm, 4 Torr pressure, 23 % radical yield [27]; assuming the same separation can be achieved with a 0.5 % energy efficient XeCl photon source

[i] MPD of $^{13}CF_3Br$ at natural abundance irradiated with a nitrogen free CO_2 laser pulse as in the present work, at 1041.3 cm^{-1} (9*P*26), 10 J cm^{-2} fluence, 10 Torr pressure [13]; assuming 5% energy efficient photon source

[j] MPD of $CF_3{}^{13}COCF_3$ at natural abundance irradiated with a normal CO_2-N_2-He laser mix, at 929 cm^{-1} (10*P*36), 6 J cm^{-2} fluence, 0.35 Torr pressure [4]; 5 % energy efficient photon source

[k] This work, from Table 1, third line; 5 % energy efficient photon source

[l] This work, from Table 1, first line; 5 % energy efficient photon source

expenditure ε in keV of photons absorbed per carbon atom produced at various product atom fractions x'. It is seen that a more selective line of lower frequency together with smaller fluences are needed for increasing values of x'. The table contains as well the length of cell L_c^{50} needed to absorb 50 % of the radiation at the specified pressure. This last column, given here to complete the picture of the selective decomposition, is self-consistent but only accurate to the extent of the accuracy of the absorption measurements and of the linear extrapolation to 50% absorption. Nevertheless, a one step product at 50% ^{13}C can be obtained at 100 Torr pressure and at moderate fluences from one of the most efficient frequencies of the CO_2 laser spectrum absorbing half of the beam energy in less than 2 m at the expense of only 0.017 keV per C-atom produced.

From this point, engineering considerations play an important role and other conditions could be prefered to that of the minimum ε. As an example, higher pressures are advantageous for two reasons, gases are easier to handle and shorter cells can be used reducing the problem of beam divergence.

Since the activation energy for $CHClF_2$ dissociation is 53 kcal mol^{-1} [23], equivalent to ~18 ir photons or 2.3 eV, values of ε look very large but, as noted previously [4], this is due to the fact that a good fraction of the energy is used for low level excitation of the undissociated ^{12}C molecules. One can visualize this as a bimodal distribution of states where the $^{13}CHClF_2$ are excited at resonance to a mean energy corresponding to $\langle {}^{13}n \rangle \gtrsim 18$ photons and that the $^{12}CHClF_2$ molecules are excited to a much lower mean energy.

Table 2 summarizes ^{13}C separation energies for a 95+ % product from various processes, independant of production rates. The purpose of this paper is not to calculate and compare production costs so only the separation energies are given. Other costs vary widely from one system to the other, for example capital equipment costs vs production rates are quite specific to each process. For production costs vs production rates for the first four processes, see [24, 25].

This comparison together with the fact that chlorodifluoromethane is an extensively used chemical makes this molecule one of the most attractive candidates to date for ^{13}C laser isotope separation. It is likely that ε can be further minimized and work is in progress using shorter CO_2 laser pulses and different substrate temperatures in order to increase the working pressure and other desirable characteristics of the process.

Conclusion

For the first time, the number of photons used and the selectivity factors in the products were measured in the same system to evaluate the effectiveness of the selective multiphoton decomposition. Chlorodifluoromethane was proven to be a very promising candidate for CO_2 laser ^{13}C enrichment after optimization of pressure of absorber, frequency and fluence of a short pulse laser field. Selectivity factors exceeding 10^3 were observed in the product tetrafluoroethylene which can be easily separated from reactants or from its own pyrolysis products [28]. The most efficient production was observed at 100 Torr pressure and the product C_2F_4 contained 50% ^{13}C and 17 eV were absorbed by the isotopic mixture at natural abundance for each C atom produced. A cell length of only 2 m would be sufficient to absorb half of the incident laser photons. Furthermore, this system provides another clear demonstration of the useful competition between collisional relaxation of ^{12}C bearing molecules and up-pumping of the same in Region I of multiphoton absorption.

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