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# Efficient multiphoton dissociation of $CF_2HCl$ in waveguide reactors with high selectivity

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**Abstract**

The feasibility of carbon-13 enrichment with high enrichment factors ($>10^2$) in waveguide reactors (WGRs) is investigated using IR laser chemistry of neat $CF_2HCl$. The performance of WGRs made of pyrex glass and gold-coated copper is evaluated under various experimental conditions and compared with that of a conventional cylindrical pyrex reactor under similar conditions. The decomposition efficiency is found to be several times better in the WGRs compared with that in the normal cell, while both the types of WGR preserve the dissociation selectivity well. The pyrex WGR seems to have an edge over the metallic version by virtue of its lower transmission losses. © 1997 Elsevier Science S.A.

*Keywords:* Multiphoton dissociation; Waveguide reactors

## 1. Introduction

Photochemical reactor design plays a crucial role in maximizing the throughput of an isotope enrichment process based on IR laser chemistry. Since the high power $CO_2$ laser-induced multiple photon dissociation (MPD) occurs mostly in the focal zone, it is essential that the isofluence region near the focus be extended by as much length as possible. This can be accomplished to a limited extent by employing a judicious combination of optical elements. However, sustained work in this area has demonstrated a much improved dissociation yield and better photon utilization based on the concept of multi-reflection cell [1–4] and waveguide (WG) reactors [5–9]. These are used for efficient isotope separation of various elements such as sulphur, carbon and hydrogen. The WG reactor (WGR) has also been employed to improve or modify the bimolecular radical reaction yield such as telomerization chemistry of $C_2F_4$ and $CF_3I$ [10].

In a hollow dielectric WG, the guide or core section has a lower refractive index than the surrounding medium. Wave guiding action occurs in the hollow WG owing to nearly total internal reflection at the dielectric surface [11]. There are several aspects such as laser beam quality, beam coupling in the WG, excitation of various WG modes, wall-induced breakdown/reaction etc. which determine the suitability of a WG as a reactor for laser enrichment of isotopes [7,8].

Kojima et al. [7] have earlier investigated carbon-13 selective MPD of neat $CF_2HCl$ in three hollow WGs made of lead glass, pyrex glass and gold-coated glass using a multimode laser. Their findings showed a four to ten times increase in the dissociation yield for photolysis in the reactor incorporating the WG compared with that excluding the WG component at the same $\beta$ level. A product enrichment factor in a moderate range of 30–50 was obtained in this study under careful conditions. A serious problem, according to this group, was the occurrence of optical breakdown which lowered the process selectivity.

Previously, we have also demonstrated a 6–7 times enhancement in dissociation yield in the case of sulphur and tritium isotope separation using WGR [8]. The present motivation is to examine several aspects of laser isotope separation in WGRs of different types and dimensions under different beam coupling conditions and to demonstrate that the high selectivity of the process can be maintained while improving the yield at the same time. The performance of the WGRs is assessed in terms of carbon-13 enrichment and the decomposition yield for the isotopically selective IR laser chemistry of neat $CF_2HCl$. Our results show that efficient MPD can be achieved in both pyrex WGR (PWGR) and gold-coated cop-


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per WGR (CWGR) retaining the high enrichment factor. For the right combination of irradiation frequency and focal fluence, enrichment factors in the range 150–200 are possible in both the WGRs. However, the PWGR seems to have a relatively superior performance compared with the CWGR by virtue of its lower beam transmission losses.

## 2. Experimental details

A commercial TEA $CO_2$ laser (Lumonics 103-2) with a repetition rate of 0.5 Hz was used for irradiation experiments. All irradiations were carried out at room temperature in the WGRs and in a conventional cylindrical pyrex cell. The laser beam (100 ns FWHM) was focused either at the WG entrance or at the centre of the conventional cell by appropriate optics. Transmission measurements were carried out with the same TEA laser and a home-made CW (1 W) $CO_2$ laser. In all these runs, a ZnSe beam splitter was used to monitor the reference beam to take care of energy/power fluctuation of the incident beam. Signal averaging (LeCroy 9450 A) for 16 shots was done for each measurement with the pulsed laser.

Precautions were taken when fabricating the WGs to make them straight and free from microbends. The internal surface finish for the metallic WGR was improved by first making an internal barrier nickel coating over which the gold coating was done. The WG section, which can be dismantled, was located symmetrically between the window sections at each end. The dimensions of the window sections were determined solely by the damage threshold of the windows which can tolerate an energy loading of 1–2 J cm$^{-2}$. The assembled WGRs were held on an optical bench which allowed adjustment of tilt and position in both horizontal and vertical planes. The WGRs were first aligned with an He–Ne laser and the final alignment was carried out by maximizing the transmitted $CO_2$ laser energy with a joulemeter. Fig. 1 shows a schematic diagram of the experimental arrangement while Table 1 describes the presently employed WGRs.

After sample irradiation, gas chromatography and mass spectrometry analyses were done for quantitative measurement of the photoproduct, i.e. tetrafluoroethylene $C_2F_4$ and its carbon-13 content. Details of the analytical procedure are given in [12]. The product enrichment factor $\beta$ is defined as

$$\beta = \frac{(C-13/C-12)\text{ ratio in } C_2F_4}{(C-13/C-12)\text{ natural ratio}} \quad (1)$$

The dissociation yield is given by

$$^{i}Y = \{1-(^{i}N_m/^{i}N_0)^{1/m}\}f \quad (2)$$

where $^{i}N_0$ and $^{i}N_m$ correspond to the concentrations of species containing isotope $i$ before and after irradiation with $m$ number of pulses respectively and $f$ is the ratio between the total reactor volume and the irradiated volume.

Table 1
Description of WGRs

| Reactor | Type | WG section | | Volume (cm$^3$) |
|---|---|---|---|---|
| | | ID (mm) | Length (cm) | |
| A | Normal cell | – | 101 | 766 |
| B | Pyrex WGR | 4 | 50 | 150 |
| C | Pyrex WGR | 4 | 103 | 155 |
| D | Copper WGR | 7 | 62 | 415 |

## 3. Results and discussion

### 3.1. Transmission studies

Different groups have investigated the propagation losses in various hollow WGs, including pyrex glass, at about 10 μm [8,13–15]. When a Gaussian beam of spot size $w_0$ at its waist is incident on the axis of the WG of radius $a$, the excited modes in the WG are only the $EH_{1m}$ modes. The optimum spot size giving the maximum transmission is dependent on the WG. For WGs with higher attenuation such as pyrex, copper or nickel, or for long WGs, the maximum transmission is attained at $(w_0/a)=0.64$ because higher order modes except for the $EH_{11}$ mode attenuate rapidly. The lowest order hybrid mode $EH_{11}$ is linearly polarized and closely resembles the $TEM_{00}$ free space Gaussian mode. Therefore, it is better for coupling to most laser output modes.

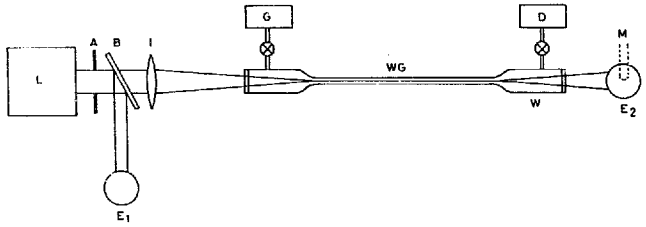


Fig. 1. Schematic diagram of the experimental set-up: L, TEA $CO_2$ laser; A, aperture; B, beam splitter; I, focusing lens; WG, waveguide section of WGR; G, gas handling system; $E_1$, $E_2$, energy meters; D, diagnostic equipment such as gas chromatograph/mass spectrometer; W, window section of WGR; M, beam profile monitor.

To obtain an idea of excitation dependent losses in WGs, we have computed theoretically and then compared the measured transmission of pyrex WGs of various bore diameters and 50 cm length at $\lambda = 10.6$ μm excited by the Gaussian mode with spot sizes $w_0 = 0.3$ and 0.4 mm [8]. The highest order mode taken for calculation was the $EH_{1,10}$ mode. We have found a good agreement between the theoretical and experimental results. However, qualities of conventional WGs for power transmission may not necessarily be applicable in the context of their use as photochemical reactors where a power density over 10 MW $cm^{-2}$ has to be handled. Therefore, we undertook transmission measurements of both the WGRs having the same length and bore diameter, using first the CW laser (conventional power transmission data) and then the TEA laser (photochemical reactor transmission data).

Our results show that using the unfocused CW laser beam at glancing angle, the transmission of both the WGRs is around 98.0% which indicates that the beam coupling into the WG as well as the surface finish are quite good. However, under focusing conditions, the transmission is reduced in both the WGs but the performance of the pyrex WG ($T = 93 \pm 1\%$) remains better than that of the metal WG ($T = 81.5 \pm 1.5\%$). It is also seen that with tighter focusing, the loss increased further. The pulsed laser measurement with focused multimode beam yielded similar results but with still lower values for the transmission ($T = 84.5 \pm 2.5\%$ for pyrex and $76 \pm 2\%$ for metal WGs).

However, use of predominantly $TEM_{00}$ mode (intracavity aperture) pulse resulted in better transmission ($T = 90 \pm 3\%$ for pyrex and $85 \pm 5\%$ for metal WGs) compared with the usual multimode beam (external aperture). In these cases, to check the mode of the WG which has been excited, the beam profiles were measured on the exit beam from the guide using a home-made thermocouple (200 μm) beam profile monitor [16]. The monitor driven by a stepper motor and controlled by a PC was used to scan the beam and a plot of the variation in intensity with radial distance was obtained. A comparison between a theoretical diffraction pattern [17] and experimental pattern observed for a well aligned, intracavity apertured condition showed that the dominant mode excited in the WG was the lowest order hybrid mode, $EH_{11}$.

This apparent difference in behaviour of the two WGs can be rationalized on the basis of the work of Hidaka et al. [15]. They have found that the oxide glass surface possesses a larger reflection coefficient for obliquely incident light than any metals near 1000 $cm^{-1}$, although the latter have higher reflection coefficients for normally incident light. It has been evaluated in this work that glass WGs can have smaller transmission losses than the metallic WGs owing to reflection of the obliquely incident light which is more or less (though not perfectly) total near 1000 $cm^{-1}$. This criterion applies regardless of the existence of $K$, the imaginary part of the complex refractive index of the material which can be related to its attenuation coefficient. Transmission characteristics thus provide useful guidelines to optimize the performance of any WGR. Although a CW-laser measurement may yield good transmission results, the performance of the WG should be evaluated with the working pulsed laser under focusing as used in the actual IRMPD experiments.

### 3.2. Isotope selective studies

The experimental results obtained can be understood in terms of the following mechanism:

$$CF_2HCl \xrightarrow[(IRMPD)]{nhv} CF_2HCl^* \quad (3a)$$

$$CF_2HCl^* \rightarrow :CF_2 + HCl \quad (3b)$$

$$2CF_2 \rightarrow C_2F_4 \quad (4)$$

$$:CF_2 + HCl \rightarrow CF_2HCl \quad (5)$$

The decomposition of $CF_2HCl$ takes place via a single product channel to give HCl and $:CF_2$ in both thermal decomposition and IRMPD [18–20]. As difluorocarbene is relatively inert, there are no complicating side reactions. It has also been established that the initial step in IRMPD of $CF_2HCl$ is the decomposition of a highly vibrationally excited molecule through a three-centre molecular elimination channel (cf. [3b]). The overall energy threshold for the process, 226 kJ $mol^{-1}$, is governed by the reaction endoergicity of 201 kJ $mol^{-1}$ and the energy barrier for recombination between HCl and $:CF_2$ (25 kJ $mol^{-1}$). Besides this, the kinetic assessment of the importance of the recombination (Eq. (5)) can be made from the relative rate of formation of $C_2F_4$, $R(C_2F_4)$ to that of $CF_2HCl$, $R(CF_2HCl)$:

$$R(C_2F_4)/R(CF_2HCl) = k_4[CF_2]^2/k_5[CF_2][HCl]$$
$$= [k_4/k_5][CF_2]/[HCl]$$

Considering that in the irradiated gas, $[CF_2]$ would be of the same order as [HCl] and taking $k_4^{300} = (1.7–2.2) \times 10^{10}$ [21], $k_5^{300} \leq 6.8 \times 10^6$ $cm^3$ $mol^{-1}$ $s^{-1}$ [22], the formation of $CF_2HCl$ by the back reaction will be negligibly small. However, under collisional conditions (~kPa), it has been shown that the vibrational energy pooling between excited $CF_2HCl$ molecules especially during the post pulse period could also lead to the formation of $C_2F_4$ [23]:

$$CF_2HCl^* + CF_2HCl^* \rightarrow C_2F_4 + 2HCl \quad (6)$$

Incidentally, this mechanism has also been shown to be highly selective and therefore may enhance the overall process yield.

We carried out our studies in a static batch mode. Typically 6.65 kPa sample was photolysed either by the 9 P(22) or 9 P(32) line of the $CO_2$ laser. These two frequencies were chosen on the basis of our earlier parametric studies in the normal cell [12]. Photolysis with the former yields good decomposition while that with the latter gives rise to large $\beta$ values. Depending on the available pulse energy, beam size and quality and the WGR type, appropriate focusing optics were employed to optimize the beam coupling and transmis-

Table 2
Photolysis conditions and results

| Run | Reactor | $f$ (cm) | $\phi_t$ (J cm$^{-2}$) | $\beta_{C_2F_3}$ | $^{13}Y$ ($\times 10^3$) | Enhancement factor |
|---|---|---|---|---|---|---|
| 1 | A [a] | 100 | 2.5 | 67 | 39.4 | – |
| 2 | D [a] | 100 | 2.6 | 80 | 43.5 | 1.10 |
| 3 | A | 50 | 3.3 | 53 | 9.6 | – |
| 4 | B | 50 | 3.6 | 40 | 19.5 | 2.03 |
| 5 | C | 50 | 3.5 | 46 | 21.8 | 2.30 |
| 6 | A | 100 | 2.1 | 305 | 5.6 | – |
| 7 | D | 100 | 2.0 | 145 | 9.7 | 1.73 |
| 8 | A [a] | 100 | 3.5 | 232 | 16.5 | – |
| 9 | D [a] | 100 | 3.5 | 222 | 25.0 | 1.50 |
| 10 | A | 50 | 6.2 | 46 | 4.0 | – |
| 11 | B | 50 | 6.4 | 49 | 11.9 | 2.97 |
| 12 | C | 50 | 6.4 | 50 | 19.0 | 4.75 |

9 P (22) line for runs 1–5 and 9 P (32) for the rest.
[a] Indicates use of an intracavity aperture. With the available optics and laser beam parameters, the ratio of focal spot size to the WG size was in the range 0.65–0.75.

sion. Photolysis conditions and results are shown in Table 2. For the pyrex WGs with narrow bore, a tight focusing optics ($f$=50 cm) was employed. This resulted in lower $\beta$ values (cf. run 3–5) compared with those from irradiation in the copper WGR wherein an $f$= 100 cm lens was used (runs 1 and 2). The $\beta$ values in our study, however, are generally better than those reported in Ref. [7] wherein a 3 mm inner diameter (ID) WG was employed. When the 9 P(32) line was used for photolysis, it resulted in still better $\beta$ values compared with those with 9 P(22) (compare runs 6–9 with runs 1 and 2) as expected. Under favourable conditions (runs 7 and 9) we could obtain $\beta$ values in the range 150–200 for the CWGR. Therefore, the present results show that efficient decomposition occurs in WGRs and selectivity is well preserved as in the normal cell runs. There is a net enhancement in the $Y$ values in the WGR case as compared with the normal cell value. This can be understood by considering the laser beam envelope in the normal and WG reactors (refer to Fig. 1 of [10]). Using a 'power-law' model [24] for IRMPD, the dissociation probability $\gamma(\phi)$ can be obtained which varies over the entire irradiation volume:

$$\gamma(\phi) = p(\phi/\phi_c)^n \text{ for } \phi < \phi_c \text{ and } = p \text{ for } \phi \geq \phi_c$$

where $n$ is an integer and has a value of about 3–4 in many IRMPD cases, $\phi_c$ is the critical fluence and $0 < p \leq 1$. Therefore, a larger irradiation volume having uniform fluence in the WG section provides the basis for enhancement of the yield.

The laser beam quality and its relative alignment with respect to the WGR were seen to be quite crucial. The experimental configuration was such that the beam waist position was located at the entrance tip of the cylindrical WG section. In some cases, owing to mismatch either during preliminary beam alignment or when the focal spot was comparable with the WG size, we observed the formation of blow-off plasma (visible light). Considering the reported high value of power density required for such a phenomenon [5], we believe that a trace of impurity might have been blown off from the surface through laser impacts to trigger the optical breakdown. After prolonged use, we did notice a faint white polymeric deposit near the entrance tip of the WG tube which could be responsible for such breakdown. It is also known that breakdown occurs more easily when the fluence and the pressure of the feed gas are higher. We took care to reject any run with repeated breakdown and a fresh run was made after thoroughly cleaning the WG section. In the rejected runs we also see that $\beta$ degraded drastically [7].

The relative yield enhancement for the presently employed waveguide reactors with respect to a normal reactor is moderate but nevertheless significant. We envisage that better results are possible with improved beam coupling and working with longer waveguides. Our primary aim was to maintain a high selectivity of the process while improving the yield at the same time. Therefore, we employed a range of focal fluences which were barely above threshold values favouring high enrichment. Even a minor reduction in the beam energy during the early passage through the WG can considerably reduce the decomposition yield for the resonantly absorbing species.

Further, there can be complications in cases where more than a single waveguide mode is excited. Under such circumstances, the available beam energy is distributed among the various modes and modifies the fluence pattern [8] so as to suppress the yield enhancement in the WG compared with a normal cell. From the irradiation and transmission measurements it appeared that the PWGR is more suitable for better photon utilization. The results obtained, therefore, are quite promising since the WGR can be readily incorporated in a flow configuration with minimum dead volume. Such a system has good potential for scaling up of the LIS.

The present work was designed to study the reaction kinetics in batch experiments in order to obtain the best performance for a chosen working molecule. In this step, controllable variables such as exciting laser frequency, pulse energy, pulse

duration, buffer gas pressure etc. are chosen to optimize the objective functions such as selectivity, yield and operating pressure. For engineering photochemistry, a study of continuous reactors will be necessary so as to minimize the deterioration of batch performance due to transmission loss, beam fluence inhomogeneity, back mixing, wall-enhanced reaction and so on. We have already modelled and discussed the beam propagation problem in WGRs [8]. Although the various intertwined parameters for the reactor design may vary from one isotope to another, one can probably take cue from the well established continuous stirred tank reactor (CSTR) approach [3,25].

## 4. Conclusions

We have shown and evaluated the suitability of two types of waveguide for use as photochemical reactors based on carbon-13 LIS from neat $CF_2HCl$ IRMPD. Under careful experimental conditions, it is possible to realize a high $\beta$ value of 150–200. Although present batch photolysis in WGRs yielded only a moderate gain in $Y$ values relative to that in a normal cell, further enhancement is possible with longer waveguides under better beam coupling.

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