

# IR laser photochemistry: Selective geometrical isomerization and collisional relaxation of *cis*-1,2-dichloro-1,2-difluoroethene

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## Abstract

The infrared multiphoton geometrical isomerization of *cis*-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> was studied under different fluences and pressures in mixtures of *cis* and *trans* isomers at a constant concentration ratio of 0.9. The absorption process was characterized phenomenologically by laser absorption cross-section measurements as a function of fluence ( $\Phi$ ) and pressure. The collisional effects on  $P(\Phi)$  were also investigated in the presence of added Ar, CO<sub>2</sub> and C<sub>2</sub>F<sub>6</sub>. A simplified master-equation formalism was applied to simulate the absorption as well as the reactive and collisional relaxation process. In the latter case information about the energy transferred per collision  $\langle \Delta E \rangle_d$  for the different colliders was obtained. © 1998 Elsevier Science S.A. All rights reserved

**Keywords:** Multiphoton processes; *Cis*–*trans* photoisomerization; IR laser photochemistry; Absorption cross section; Collisional deactivation

## 1. Introduction

Infrared multiphoton excitation (IRMPE) processes have been the subject of many theoretical and experimental works since the first observations of chemical reactions induced by infrared lasers [1–6]. The phenomenological characterization of this process involves absorption cross section and reaction probability measurements at different pressures and laser fluences. IRMPE research was encouraged by the possibility to produce a selective bond cleavage upon irradiating at a resonant vibrational frequency. However, energy randomization is too fast and consequently reaction is statistical. In spite of this, the interest in these processes lies in the possibility to induce selective reactions in mixtures with different compositions. The selectivity of the process is given by the fact that, in a gas mixture, only the species with a moderate absorption at the excitation wavelength will be excited above the reaction threshold. This effect could be used to isolate compounds with similar physical properties, as it is usually the case in the synthesis of isomeric mixtures which are very difficult to separate by standard methods, such as *cis* and *trans* isomers. IRMPE could, in principle, induce the geometrical isomerization of only one of the isomers. The few studies of geometrical isomerizations induced by IRMPE has been limited to measurements of the reaction probability

for isomerization in competition with dissociation reactions [7–9]. In almost all of them the absorption process has not been characterized.

One of the aims of this work was to induce a clean selective isomerization in a mixture without producing any dissociation reaction that would result only in material loss and undesirable side products. In order to achieve this, it is necessary to find the experimental conditions which allow for a proper control of the absorption and reaction processes (mainly fluence and pressure) in order to achieve the highest yield without producing fragmentation.

One of the main factors affecting selectivity is the temperature increment of the gas mixture through collisional transfer of the absorbed energy to the bath gas, which results in post-pulse thermal reactions. The temperature change can be controlled by the addition of inert gasses in order to increase the heat capacity of the mixture but this is detrimental to the reaction yield due to collisional deactivation of vibrationally excited molecules. Pressure also has an influence on the absorption process since collisions contribute to the removal of anharmonic and rotational bottlenecks, increasing in this way the number of photons absorbed per molecule. However, at high pressures, collisional relaxation competes with the rate of laser absorption preventing excitation at energies above the reaction threshold. This makes it necessary to study the effect of pressure of various gases to find the conditions for maximum efficiency.

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A useful characterization of multiphoton processes is obtained by model simulation using a master-equation formulation of the various rate processes involved. Adequate parametrization can produce a reasonable description of the effect of fluence and pressures on reaction yields and absorption cross sections [10]. This approach involves the postulation of a model for the microscopic absorption cross sections to simulate the experimental measurements [10–13].

The molecule selected for our purposes is the *cis*-1,2-dichloro-1,2-difluoroethene because it presents absorption at  $948\text{ cm}^{-1}$ , resonant with the P(14) line of the  $\text{CO}_2$  laser. The *trans* isomer is transparent at this irradiation wavelength, so it is possible to produce a selective excitation of the *cis* isomer and eventually induce its geometrical isomerization.

## 2. Experimental

The irradiation source was a pulsed TEA high powered tuneable  $\text{CO}_2$  laser (Tachisto Laser Systems) model 217b, pulse width 40 ns FWHM, 500 ns tail. The laser was tuned to the P(14) line at  $948.8\text{ cm}^{-1}$ , near the maximum of the absorption band of the *cis* isomer (Fig. 1). The laser beam was slightly focused by means of a Galilean telescope using  $\text{BaF}_2$  lenses in order to increase fluence.

A mixture of *cis*- and *trans*-C<sub>2</sub>F<sub>2</sub>Cl<sub>2</sub> in a 0.9 concentration ratio was obtained from Pierce Chem. Its purity was checked by gas chromatography and by FTIR spectroscopy. The samples were degassed, distilled under vacuum and stored in a Pyrex bulb.

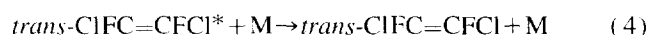
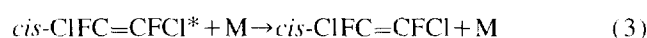
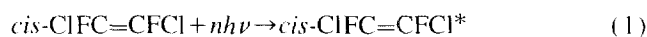
The experiments for measuring the reaction probabilities were performed using cylindrical reaction vessels, 5 cm long, constructed from 3.5-cm-diameter Pyrex tubing with planar NaCl windows. The cells were evacuated to  $10^{-5}$  Torr before each experiment. Pressures were measured with a capacitance manometer with a sensitivity of 0.001 torr. The laser pulse energy was measured with a Scientech calorimeter model 362. The beam profile was monitored via burn patterns on heat-sensitive paper. This method of measuring the area introduced an estimated error on the calculation of the value of fluence of about 10%. The laser line was tuned with the help of a laser spectrum analyser (Optical Engineering). Reaction product mixtures were analysed by FTIR spectroscopy and by gas chromatography using a 6.0-m column of 5% DMSO on alumina and a thermal conductivity detector. The laser absorption cross sections  $\sigma_L(\phi)$ , as defined by Beer's law, were obtained from the energy measurements with a dual pyroelectric arrangement (Laser Precision models RJP 735 and JP 735) using a 1.0-m optical path cell. Measurements were made first with the empty cell to account for window losses and then with the sample at the desired pressure.

## 3. Results

### 3.1. Reaction measurements

Selective irradiation of the *cis* isomers at  $948.8\text{ cm}^{-1}$  in a mixture of *cis*- and *trans*-C<sub>2</sub>F<sub>2</sub>Cl<sub>2</sub> results in a clean, pressure dependent, geometrical isomerization, as determined by IR and gas chromatography analysis. A typical FTIR spectrum at a total pressure of 1.0 Torr of the mixture before and after laser irradiation at a fluence of  $5.0\text{ J/cm}^2$  is shown in Fig. 1 where the absorption bands corresponding to each isomer are also indicated.

The overall process can be described by the following reaction mechanism:



Process (1) corresponds to multiphoton absorption of  $n$  infrared photons yielding a vibrationally excited molecule of the *cis* isomer. If the absorbed energy is higher than the reaction threshold for isomerization, reaction (2) will occur to produce an excited molecule of the *trans* compound, which can revert to the original isomer. Steps (3) and (4) represent collisional deactivation processes.

Two different series of experiments were made. In one of them, the total pressure of the *cis*-*trans* mixture was varied in the range 0.1 to 3.0 Torr, with incident fluences between 0.8 and  $5.1\text{ J/cm}^2$ . In the other series the experiments were performed at  $3\text{ J/cm}^2$  and 1.0 Torr of the mixture with the addition of inert gases (Ar,  $\text{CO}_2$  and  $\text{C}_2\text{F}_6$ ) at various pressures. In all the experiments the sample was irradiated with a minimum of 1000 laser pulses in order to obtain an appreciable isomerization yield.

The reaction probability per pulse was calculated according to the following equation [12]:

$$P(\phi) = \frac{V_0}{V_i} \left( 1 - \frac{C_0}{C_n} \right)^{\frac{1}{n}} \quad (5)$$

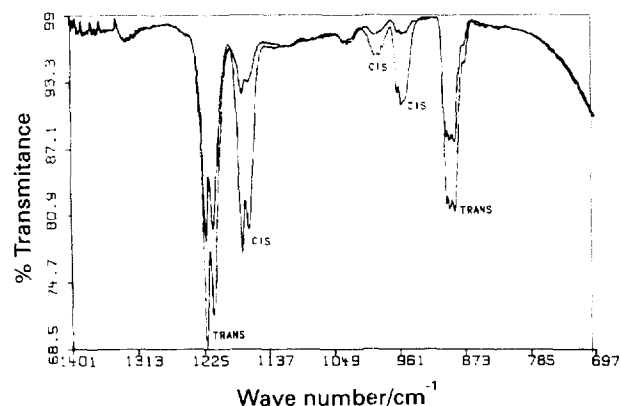


Fig. 1. Infrared spectra of 1.2 Torr of a mixture of *cis*- and *trans*-C<sub>2</sub>F<sub>2</sub>Cl<sub>2</sub> before and after laser irradiation with 1200 pulses at  $5.1\text{ J/cm}^2$ .

where  $V_i$  and  $V_0$  are the irradiated and the cell volumes respectively,  $C_n$  is the concentration of the *cis* isomer after irradiation with  $n$  pulses. For the parallel geometry used,  $V_0/V_i = (d_0/d_i)^2$  where  $d_0$  and  $d_i$  are the cell and beam diameters respectively. The  $V_0/V_i$  ratio was:  $10 \pm 1$  for  $\Phi = (0.8 \pm 0.1)$  J/cm<sup>2</sup>,  $11 \pm 1$  for  $\Phi = (1.7 \pm 0.2)$  J/cm<sup>2</sup>,  $18 \pm 2$  for

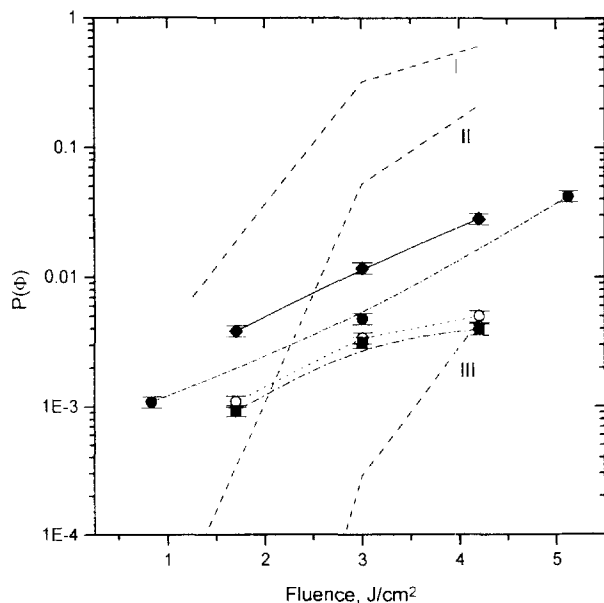


Fig. 2. Dependence of the reaction probability per pulse with fluence at different pressures of ClFC=CFCl: (♦) 0.5 Torr, (●) 1.2 Torr, (○) 1.5 Torr, (■) 2 Torr. Model calculations of the reaction probability per pulse, under collisionless conditions, for different exponents  $n$  of the absorption cross-section model (Eq. (10)), are shown as dashed lines: I:  $n=0.5$ ; II:  $n=0.7$ ; III:  $n=1.0$ .

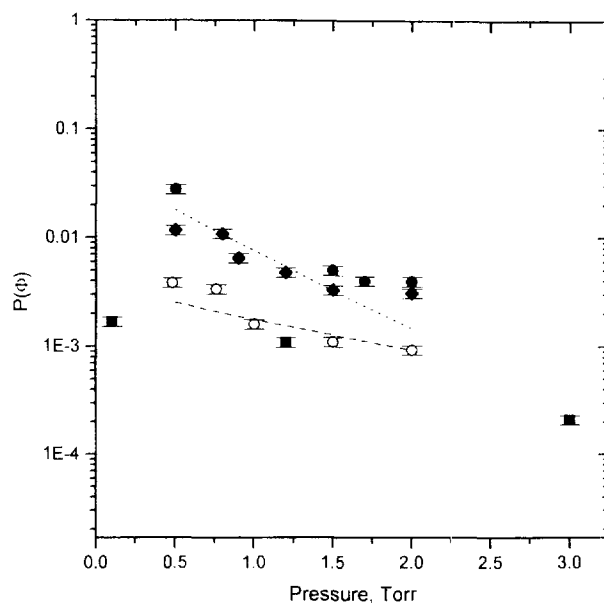


Fig. 3. Dependence of the reaction probability per pulse with pressure at different fluences: (●) 4.2 J/cm<sup>2</sup>, (♦) 3.0 J/cm<sup>2</sup>, (○) 1.7 J/cm<sup>2</sup>, (■) 0.8 J/cm<sup>2</sup>. Model calculations for the collisional deactivation of *cis*-ClFC=CFCl with  $\langle \Delta E \rangle_d = 1896$  cm<sup>-1</sup> (.....) at 3 J/cm<sup>2</sup> and with  $\langle \Delta E \rangle_d = 395$  cm<sup>-1</sup> (—) at 1.7 J/cm<sup>2</sup> are also shown.

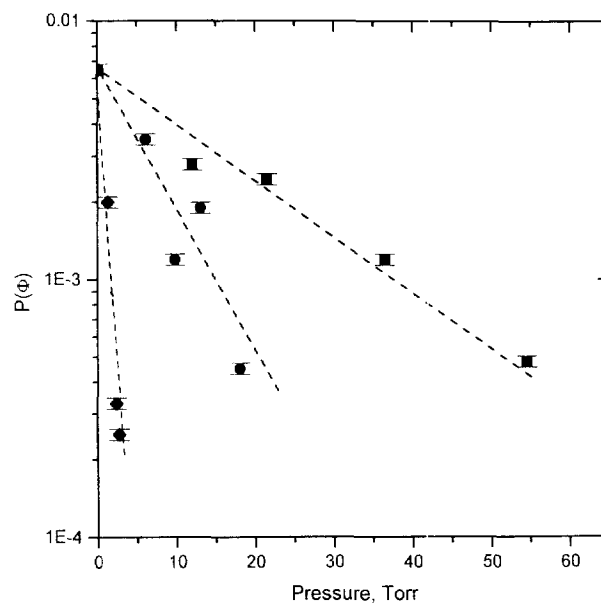


Fig. 4. Reaction probability of 1.2 Torr of the mixture of *cis*- and *trans*-ClFC=CFCl as a function of added pressure of (■) Ar, (●) CO<sub>2</sub>, (♦) C<sub>2</sub>F<sub>6</sub>, at a fluence of 3 J/cm<sup>2</sup>. Calculations with the master equation are shown as dashed lines.

$\Phi = (3.0 \pm 0.3)$  J/cm<sup>2</sup>,  $25 \pm 3$  for  $\Phi = (4.2 \pm 0.4)$  J/cm<sup>2</sup> and  $30 \pm 3$  for  $\Phi = (5.1 \pm 0.5)$  J/cm<sup>2</sup>.

The isomerization probability per pulse was independent of the number of laser shots, between 1000 and 5000 pulses, as observed experimentally.

The fluence dependence of the reaction probability at four different pressures are displayed in Fig. 2. The results show that the fraction of *cis*-ClFC=CFCl isomerized per pulse increases with fluence and decreases with pressure. Even at the highest fluence used (5.1 J/cm<sup>2</sup>) the reaction probability is low, which makes it necessary to use a large number of laser pulses to produce a substantial enrichment of the *trans* isomer. Thus, at a fluence of 5.1 J/cm<sup>2</sup>, irradiation with 4500 pulses is needed to produce a sample with 99% of the *trans* isomer.

The effect of total pressure on the reaction probability at different fluences is plotted in Fig. 3. The reaction probability decreases with total pressure of the *cis*-*trans* mixture and pressure of added bath gases (Figs. 3 and 4) and depends on the complexity of the bath gas. This result indicates the different efficiencies of Ar, CO<sub>2</sub> and C<sub>2</sub>F<sub>6</sub> in deactivating vibrationally excited ClFC=CFCl.

### 3.2. Cross-section measurements

The average number of photons absorbed per molecule,  $\langle n \rangle$ , is related to the laser absorption cross sections according to:

$$\langle n \rangle = \frac{\sigma_L(\Phi) \cdot \Phi}{h\nu} \quad (6)$$

where  $\Phi$  is the incident fluence,  $\sigma_L(\Phi)$  is the laser absorption cross section and  $h\nu$  is the energy of the laser photon.

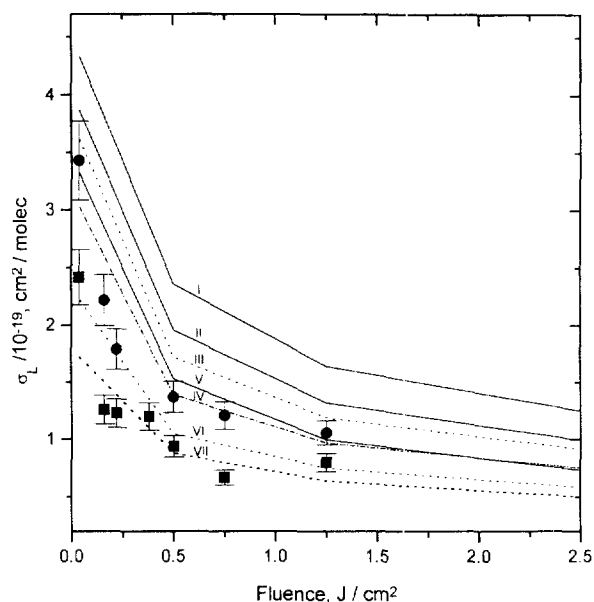


Fig. 5. Dependence of the laser absorption cross section with fluence at different pressures of ClFC=CFCl: (●) 0.47 Torr, (■) 0.22 Torr. Model calculations of the laser absorption cross sections for different exponentials  $n$  and different fractions of absorbing molecules,  $f$ , are also shown: I:  $n=0.5$ ,  $f=1.0$ ; II:  $n=0.7$ ,  $f=1.0$ ; III:  $n=0.5$ ,  $f=0.5$ ; IV:  $n=1.0$ ,  $f=1.0$ ; V:  $n=0.5$ ,  $f=0.4$ ; VI:  $n=0.5$ ,  $f=0.2$ ; VII:  $n=0.5$ ,  $f=0.1$ .

In order to characterize the absorption process  $\sigma_L(\Phi)$  was measured as a function of laser fluence and pressure. Unfortunately, measurement with cells shorter or larger than 1 m could not be made. However, due to the small value of  $\sigma_L$ , the fluence variation across the absorption cell is very low and we assume that it has no influence on the experimental results.

The absorption cross section decreases with fluence, as shown in Fig. 5. The effect of pressure was also investigated. The results obtained at a constant fluence of 1 J/cm<sup>2</sup>, for different pressures of neat ClFC=CFCl and with added Ar are shown in Fig. 6a and b respectively. In both cases the absorption cross section increases with pressure, which results in a higher average number of photons absorbed per molecule. However, this larger amount of energy taken by the sample does not result in an increment of the reaction probability, as it decreases with pressure. The lower efficiency of laser photons in promoting the reaction implies that either energy is transferred to cold molecules during the absorption process producing a decrease in the fraction of molecules that reaches the reaction threshold, or that molecules with enough energy to react are collisionally deactivated.

#### 4. Modelling the IRMPE process

The evolution of the population of molecules under IR laser irradiation can be described by a set of coupled rate equations [10–15]:

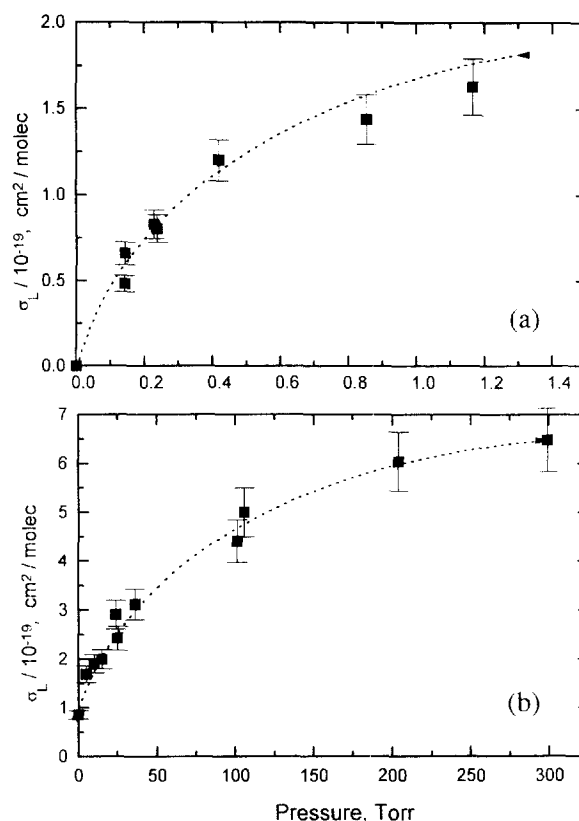


Fig. 6. Dependence of the absorption cross section at a fluence of 1 J/cm<sup>2</sup> with: (a) ClFC=CFCl pressure (b) Ar pressure (the ClFC=CFCl pressure is 0.220 Torr).

$$\frac{dC_i}{dt} = I(t) [\sigma_{i,i+1}C_{i+1} + \sigma_{i,i-1}C_{i-1} - (\sigma_{i+1,i} + \sigma_{i-1,i})C_i] + \omega \sum_j P_{ij}C_j - \omega C_i - k_i C_i + k_i' T_i \quad (7)$$

and

$$\frac{dT_i}{dt} = \omega \sum_j P_{ij}T_j - \omega T_i - k_i' T_i + k_i C_i \quad (8)$$

where  $C_i$  and  $T_i$  represent the population of level  $i$  for the cis and trans isomers respectively,  $I(t)$  is the intensity profile of the laser pulse,  $k_i$  and  $k_i'$  are the microscopic rate coefficients for the cis–trans and trans–cis isomerization respectively,  $\sigma_{i+1,i}$  is the cross section for absorption from level  $i$  to level  $i+1$ , related by detailed balance with the cross section for the emission from level  $i+1$  to  $i$ ,  $P_{ij}$  is the collisional transition probability from level  $j$  to level  $i$  and  $\omega$  is the collisional frequency. The same values of  $P_{ij}$  for both isomers are used.

Evaluation of  $k_i$  and  $k_i'$  requires knowledge of the Arrhenius parameters for the isomerization reaction [16,17]. As this information is not available they were estimated by comparison with the parameters of cis–trans isomerization reactions of related compounds. In a systematic series of shock-tube isomerization studies, Jeffers [18] investigated the effect of halogenation and size in the cis–trans isomeri-

zation of different olefins. The activation energies corresponding to halogenated species are all around  $20,000 \pm 1000 \text{ cm}^{-1}$  and the preexponential factors are  $\log(A) = 13.7 \pm 0.4 \text{ s}^{-1}$ . Since the enthalpy change for the cis–trans isomerization of C1FC=CFCl has been estimated to be practically zero [19], we have adopted a value of  $E_a = 19600 \text{ cm}^{-1}$  and  $\log(A) = 13.5 \text{ s}^{-1}$  for both direct and reverse processes.

The density of states  $\rho(E)$  was calculated by exact count [20]. The collisional transition probabilities  $P_{ij}$ , were calculated using a stepladder model, which is less computationally demanding and produces similar results than more realistic models [21,22], at least for the present purposes:

$$P_{ij} = 1 - P_{ji} \text{ for } i-j = \langle \Delta E \rangle_d, P_{ij} = 0 \text{ for } i-j \neq \langle \Delta E \rangle_d \quad (9)$$

where  $\langle \Delta E \rangle_d$  is the average energy transferred per deactivating collision.

The upward transition probabilities were calculated by detailed balance and the normalization condition. The collisional frequencies and the Lennard–Jones parameters used in the calculations are shown in Table 1.

The microscopic absorption cross sections for the absorption from level  $i$  to  $i+1$  of the type were calculated according to the following model:

$$\sigma_{i+1,i} = \frac{\sigma_{10}}{(i+1)^n} \quad (10)$$

where  $\sigma_{10}$  is the absorption cross section for the  $1 \rightarrow 0$  absorption as determined by conventional IR spectroscopy at  $948.5 \text{ cm}^{-1}$ , equal to  $6.5 \times 10^{-19} \text{ cm}^2$ , and  $n$  is a variable parameter adjusted to reproduce the experimental laser absorption cross-section results.

The experimental laser absorption cross sections were modelled, in collisionless conditions, varying the exponent of Eq. (10) between 0 and 1. The calculated results qualitatively reproduce the effect of fluence (Fig. 6). The best agreement is obtained with  $n = 1$ , but in this case the calculated reaction probabilities significantly differ from experiment (Fig. 2).

The above results suggest that only a fraction of molecules,  $f$ , interacts with the laser radiation while the remaining fraction  $1-f$  remains inactive. When this effect is incorporated in the calculations and the absorption cross sections are modelled in collision free conditions the best fit to the experimental results is obtained with  $n = 0.5$  and  $f = 0.2$  (Fig. 5).

When collisions are relevant to the multiphotonic process, intermolecular rotational and vibrational relaxation occur and

both have to be considered into the model calculations. In order to introduce rotational relaxation it must be considered that, in the absence of collisions during the laser pulse, the molecules are promoted to excited levels burning a rotational hole in the fundamental vibrational energy level. This hole is filled through rotational relaxation via a rate process that must be added to the master equation (Eqs. (3) and (4)):

$$\frac{dN_1}{dt} = k_{\text{rot}}(N_1^* - N_1^{\text{eq}})N_1 \quad (11)$$

In this equation  $N_1$  is the total density of molecules,  $k_{\text{rot}}$  is a phenomenological rate coefficient for the rotational hole filling (not necessarily a true rate constant),  $N_1^*$  is the population of molecules in the fundamental vibrational energy level that are not in resonance with the laser and  $N_1^{\text{eq}}$  is the same number but in the case that a Boltzmann distribution would have been reestablished. The value of  $k_{\text{rot}}$  is another parameter that was varied in the modelling calculations [10].

The collisional deactivation process is included in the master equation using the transition probability matrix  $P_{ij}$  which depends parametrically on  $\langle \Delta E \rangle_d$ . With  $k_{\text{rot}} = 4.5 \times 10^{-5} \text{ ns}^{-1} \text{ Torr}^{-1}$  and the same fraction of molecules,  $f = 0.2$ , it was found that a value of  $\langle \Delta E \rangle_d = 1896 \text{ cm}^{-1}$  fits satisfactorily the experimental data at a fluence of  $3.0 \text{ J/cm}^2$  and  $\langle \Delta E \rangle_d = 395 \text{ cm}^{-1}$  at a fluence of  $1.7 \text{ J/cm}^2$ , as shown as dotted lines in Fig. 3.

The experiments performed with the olefin diluted in an inert bath gas were simulated taking into account self-collisional relaxation and deactivation caused by added bath gases. As the value of  $\langle \Delta E \rangle_d$  for self relaxation was obtained from the above simulations ( $\langle \Delta E \rangle_d = 1896 \text{ cm}^{-1}$ ) at the same fluence, the parameter to be varied to fit the experiments is the value of  $\langle \Delta E \rangle_d$  for the energy transfer process between the olefin and the bath gas. Calculations with the values of  $\langle \Delta E \rangle_d$  that best reproduce the experimental reaction probabilities as a function of pressure are shown as dashed lines in Fig. 4. The values of  $\langle \Delta E \rangle_d$  are  $158 \text{ cm}^{-1}$  for Ar,  $316 \text{ cm}^{-1}$  for  $\text{CO}_2$  and  $2894 \text{ cm}^{-1}$  for  $\text{C}_2\text{F}_6$ .

## 5. Conclusions

A selective enrichment of a sample containing a mixture of cis and trans isomers can be accomplished by IRMPD by selectively inducing the cis–trans isomerization.

The multiphoton absorption process seems to be highly inefficient since only a fraction of molecules can be pumped to higher levels according to the master-equation simulations.

Master-equation calculations show that a model in which the absorption cross section decreases with the level of excitation is appropriate to simulate the dependence of both the reaction probabilities and absorption cross sections on fluence and pressure.

The effect of collisions is complex. They enhance the absorption process through rotational hole filling but they are detrimental to the reaction yield because of collisional deac-

Table 1  
Collisional frequencies  $\omega_{A-M}$  and collision integrals for the different collisional partners

A	M	$\omega_{A-M} (10^7 \text{ s}^{-1})$	$\Omega_{A-M}^{2,2}$
C1FC=CFCl	Ar	1.16	1.25
	$\text{CO}_2$	1.43	1.49
	$\text{C}_2\text{F}_6$	1.35	1.50
	C1FC=CFCl	1.5	1.58

tivation of vibrationally excited molecules above threshold. The increasing value of  $\langle \Delta E \rangle_d$  when fluence changes from 1.7 J/cm<sup>2</sup> to 3 J/cm<sup>2</sup> indicates a dependence on vibrational excitation. The dependence of  $\langle \Delta E \rangle_d$  with the complexity of the collisional partner is evidenced in the series Ar, CO<sub>2</sub>, ClFC=CFCl and C<sub>2</sub>F<sub>6</sub> where the corresponding  $\langle \Delta E \rangle_d$  values increase with the number of vibrational degrees of freedom and molecular weight.

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