A BOTTLENECK EFFECT IN PERFLUOROPROPENE

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By investigating the infrared dissociation yield of perfluoropropane under a convenient range of experimental conditions on pressure, laser fluence and number of irradiation shots, we have seen that i) besides the already known final products, C2F and C2F6, the dissociation of this molecule also produces polytetrafluoroethylene, and ii) contrary to what one should expect from its rather large molecular size, perfluoropropane opposes a strong bottleneck effect against absorption of resonant infrared radiation, at least for irradiation fluences smaller than ≈ 1.8 Jcm⁻².

KEY WORDS: Infrared Multiphoton Dissociation; Perfluoropropane; Polytetrafluoroethylene; Bottleneck effect.

1 INTRODUCTION

Infrared multiphoton dissociation of perfluoropropane has been studied by Nip and col.¹ and by Santos and col.² These works have established that the most probable mechanism for the dissociation reaction is

\[ C_3F_6 \rightarrow C_2F_4 + CF_2 \]

\[ 2CF_2 \rightarrow C_2F_4. \]  

It was also pointed out that some amount of C2F6 is also produced in the reaction in such a way that the more initial pressure of C3F6, the larger proportion of C2F6 is formed. Also was suggested¹ that CF3 is produced when two “hot” CF2 radicals react

\[ 2CF_2^* \rightarrow CF_3 + CF. \]  

However, it is not quite clear how the resulting CF radicals could finally appear.

In the present note we reexplore the multiphoton dissociation process of perfluoropropane when it is irradiated with one single resonant wavelength. Results for the pressure and number of shots dependence of the dissociation yield and final reaction products suggest that, depending on the fluence of the irradiation, it is possible to distinguish two different behaviours in the dissociation of perfluoropropane.
Evidence is also presented for the presence of a new product formed under all studied experimental conditions.

2 EXPERIMENTAL

All experiments were performed with a TEA–CO$_2$ laser (lumonics K-103), equipped with a frontal multimode optics and a diffraction grating blazed at 10.6 $\mu$m, operating with a typical CO$_2$–N$_2$–He (8–8–84) mixture to give pulses of approximately 65 ns peak followed by a tail of about 1.5 $\mu$s. In all experiments the laser line R(34) at 9.603 $\mu$m was used. This line nearly coincides with the linear absorption maximum at 1036 cm$^{-1}$ corresponding to the C–F stretching vibration of the central carbon atom in the C$_3$F$_6$ molecule.

The experiments were carried out in a pyrex cell 9.5 cm long with a total volume of 71 cm$^3$ equipped with NaCl end windows. A nearly parallel geometry was employed by inserting a 2 m focal lens between the laser and the cell and different values of the incident fluence were obtained by varying their relative position. The energy was changed by placing CaF$_2$ plates and/or polyethylene films in the optical path controlling on the high voltage settings of the laser for a finer adjust. The fluence values were determined by the measured pulse energy divided by the laser beam pattern area produced on thermal printer paper. The estimated uncertainty in the absolute fluence is around $\pm$15%. A pyroelectric detector Lumonics 20D was used to measure the incident pulse energy, and a photon drag detector (Rofin, model 7415) to check the time profile of the pulses.

Dissociation yield measurements in the parent molecule and in the resulting products were carried out by infrared spectroscopy by using a Perkin-Elmer FTIR spectrophotometer 1725X. The study of the influence of the different experimental parameters in the reaction was made possible by introducing the two dimensionless parameters:

$$\alpha_1 = \frac{\text{Absorbance of the C}_2\text{F}_6 \text{ band at 1251 cm}^{-1}}{\text{Change of the absorbance of the C}_3\text{F}_6 \text{ band at 1036 cm}^{-1}}$$

and

$$\alpha_2 = \frac{[\text{C}_2\text{F}_4]}{1.5[\text{C}_3\text{F}_6]},$$

where $\Delta$[C$_3$F$_6$] is the change in the concentration of this molecule due to dissociation, $\alpha_1$ is proportional to the relation between the concentration of formed C$_2$F$_6$ and the consumed C$_3$F$_6$ and $\alpha_2$ gives the proportion of dissociated C$_2$F$_6$ transformed in C$_2$F$_4$, $\alpha_2 = 1$ means that all formed CF$_2$ radicals are transformed in C$_2$F$_4$. The actual concentration of C$_2$F$_4$, was determined by calibrating its absorption band at 1187 cm$^{-1}$ using the stoichiometry of the single channel multiphoton dissociation reaction.
2CF₂HCl + nhv → C₂F₄ + 2HCl

Perfluoropropene gas sample was kindly supplied by Prof. H. van den Bergh, and was used without further purification.

3 RESULTS AND DISCUSSION

For quantifying the dissociation yield we have used the fraction of C₃F₆ molecules dissociated per laser pulse, in the irradiated volume, \( f \), defined by

\[
f = \frac{V_C}{V_i} \left( 1 - \left( \frac{[C_3F_6]_0}{[C_3F_6]} \right)^n \right)
\]

where \( V_C \) is the cell volume, \( V_i \) is the irradiated volume, \( n \) is the number of laser pulses and \([C_3F_6]_0\) and \([C_3F_6]_0\) are, respectively, the C₃F₆ concentration before and after the irradiation with \( n \) laser pulses.

For \([C_3F_6]_0 = 6.10^{-6} \text{ mol/l}\), using 10 laser shots per experiment, the obtained \( f \) shows a typical strongly fluence-dependent pattern, with a dissociation threshold at around 1.2 J/cm² which saturates at \( f \approx 0.45 \) for \( \varphi \geq 4.4 \text{ J/cm}^2 \). It has been also shown, for the above conditions, that both parameters \( \alpha_1 \) and \( \alpha_2 \) vary in a nearly but opposite linear way with fluence, with a positive slope for \( \alpha_1 \), meaning a favouring of C₂F₆ formation against C₂F₄ as fluence increases.

![Figure 1](image-url)  
**Figure 1** Fraction, \( f \), of C₃F₆ molecules dissociated per laser pulse vs. \([C_3F_6]_0\). Curves a) and b) were obtained with 10 laser pulses and curve c) with 50 laser pulses.

Figure 1 shows how the fraction \( f \) behaves with \([C_3F_6]_0\). Depending on the fluence being used, two different behaviours appear. For the larger fluences (Figure 1a), \( f \) first continuously decreases until an initial concentration of around \( 10^{-5} \text{ mol/l} \), keeping a rather constant value thereafter. The behaviour for smaller fluences (Figure 1b), is in
fact quite different after initial concentration an 10⁻³ mol/l, for f then clearly increases
along the explored concentration interval. This behaviour becomes more apparent
when a larger proportion of the molecules in the cell are irradiated (Figure 1c); in this
case the plot also tends to saturate from below at the largest concentration. These
results complete, in the low concentration region and at low fluences, our previous
ones².

The formation of final products can be followed by giving the variation of the
parameters α₁ and α₂. In Figure 2 we represent the variation of these parameters vs.
[C₃F₆]₀ for the three values of fluence used in Figure 1. It can be observed that
whereas α₂ remains nearly unchanged, α₁ increases with [C₃F₆]₀ at rates which tend
to be larger for lower fluences. These results could not be satisfied by invoking just
the proposed mechanisms (1) and (2) for dissociation and/or recombination of the
fragments.

![Figure 2 Parameters α₁ and α₂ vs. [C₃F₆]₀ for the three curves shown in Figure 1. 10 pulses were used in all the experiments.](image)

The dependence of the dissociation yield of C₃F₆ on the number of irradiation
pulses for two different conditions of fluence and initial concentration of C₃F₆ have
also been studied. In all the cases f decreases with the number of pulses, the lower
the fluence the quicker the decrease. Both α₁ and α₂ decrease when increasing the
number of pulses, with the largest relative decrease being obtained for the highest
fluence and smallest initial concentration (Figure 3). Again this result do not fit the
proposed dissociation and/or recombination mechanisms.

As we have pointed out above, from the parameters α₁ and α₂ we can quantify
the exact amounts of C₂F₄ but not the C₂F₆ quantity formed in the dissociation
process; however, we can still measure the relation between the variations in α₁
and α₂ for different points of a given plot. This has been carried out for the different
experimental curves comparing the results with that would be predicted for the
variations of α₁ and α₂ if just reactions (1) and (2) were operating. Once again,
and quantitatively this time, we have obtained that (1) and (2) fail to describe
Figure 3 Parameters $\alpha_1$ and $\alpha_2$ vs. the accumulated number of pulses for two different conditions of fluence and $[C_3F_6]_0$.

consistent with this conclusion is the presence of a new dissociation product, so far unnoticed, which we have uncovered by performing a closer inspection of the infrared spectra. In fact, the infrared spectrum recorded on a carefully evacuated reaction cell, (Figure 4), presents two absorption features centered at around 1150 and 1210 cm$^{-1}$. We have identified these absorptions to the presence of polytetrafluoroethylene, $(CF_2-CF_2)_n$, a solid polymer whose occurrence has been only reported, to the extent we know, in dissociation experiments of $CF_2HCl$ by a continuous discharge CO$_2$ laser$^7$, and constituted an interesting finding in glass etching initiated by excimer laser photolysis of CF$_2$Br$_2$.$^8$

It is difficult to exactly measure the proportion of polymer formed in the dissociation of a definite amount of C$_3$F$_6$, due to the fact that we do not know how the polymer layer is distributed on the walls of the reaction cell. However, an estimate of the proportion of C$_3$F$_6$ transformed in polymer can be done from the absorption coefficient given in the literature$^6$, assuming an uniform distribution of the newly formed polymer on the cell walls. Thus, a proportion of around 20% of the dissociated C$_3$F$_6$ transformed into $(CF_2)_n$ has been obtained for experiments of Figure 1a. Of course, one should take into account the formation of the polymer for such a high proportion.

One interesting point is to elucidate of how this compound is produced. One can imagine two extreme situations for which a) it might be formed through a secondary process from the CF$_2$ radicals (or mixture of CF$_2$ and C$_2$F$_4$) produced in the dissociation process or, b) it might be directly created from the excited C$_3$F$_6$. Using the $\alpha_1$ and $\alpha_2$ values obtained from the different experiments, we have found conversions of C$_3$F$_6$ into $(CF_2)_n$ in both extreme situations, that are in agreement with the quantity estimated above from the infrared spectra. These results suggest that these two mechanisms would probably contribute the real C$_3$F$_6$ dissociation and recombination processes. On the other hand, the fate of CF radicals could well be interwoven with the formation of the long polymer chains and, if the polymer chains would actually incorporate most of the formed CF radicals, then one could explain the lack of gaseous compounds
containing CF, at the cost of very slight changes in the infrared absorption features of the polymer.

The obtained results for the dependence of \( f \) versus the initial concentration of \( C_3F_6 \), number of pulses and fluence, when this last parameter is kept above 2.4 J/cm\(^2\) (Figures 1b and 3), are as one should expect for a rather big molecule\(^9\): a decrease and subsequent saturation of \( f \) when the initial concentration is increased and a fairly high dissociation probability obtained for moderate fluences. In principle, though these results would be taken as a proof for the lack of any bottleneck effect during energy absorption, the increase in the dissociation yield when the initial concentration of \( C_3F_6 \) raises from \( 10^{-5} \) to \( 10^{-4} \) mol/l at low fluences (Figure 1b and c) points out to the existence of some kind of bottleneck against the absorption process. This bottleneck, produced by the large anharmonicity of the active mode, would operate just above the few first transitions before the large density of vibrational and rotational levels couple to form the quasicontinuum. This effect would manifest only when the irradiation of the molecules is made at low values of fluence, becoming indetectable for fluences larger than 2.4 J/cm\(^2\). In this way, the fluence becomes a crucial parameter when one is trying to classify the molecules in small or large respect to the dissociation.

The trends exhibited in Figure 1 can be now easily explained. At both fluence regimes, shown in Figure 1a and b, in the low pressure region where the time between collisions
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is larger than the time pulse but smaller than the time needed for the dissociation process to be completed\textsuperscript{10}, the collisions prevent the dissociation of C\textsubscript{3}F\textsubscript{6} to occur. The larger the proportion of irradiated molecules, the clearer is this effect shown. When the pressure is high enough for the molecules to collide within the time pulse, the bottleneck effect, present in the low fluence experiments, is overcome by the effect of these collisions\textsuperscript{11}, increasing the fraction of molecules with the ability to proceed absorbing laser photons. It follows that collisions have two opposite effects on the dissociation yield. Assuming that there are no V–T relaxation at the minimum of Figure 1b and c, and, hence, that molecules possess a thermal mean velocity at room temperature, we can estimate that, even for an effective pulse width of 1 \( \mu \)s, the number of collisions at the minimum concentration is as long as 1 \( \mu \)s\textsuperscript{-1} in the hard-sphere approximation\textsuperscript{12}, that is a high efficiency of collisions in removing the bottleneck effect present in this molecule when is irradiated at low fluence.

Other mechanisms increasing the decomposition yield with pressure, such as vibrational energy pooling and rotational hole filling should also be considered\textsuperscript{11}. Nevertheless, experiments carried out in our laboratory for multiphoton dissociation of several initial concentrations of C\textsubscript{3}F\textsubscript{6} in the presence of Ar\textsuperscript{13} have shown a noticeable decrease of the yield along the Ar pressure interval 0–3 millibars. Actually, the larger the initial concentration of the parent molecule the smaller the inhibitory influence of the buffer gas. These results seems to confirm that the importance of a possible rotational hole filling is very small compared to the circumvention of the anharmonic bottleneck effect through homogeneous collisions. The contribution of a VV energy pooling mechanism to the increase of the yield is rather difficult to evaluate. The results obtained for the higher fluence values (Figure 1a and b) indicates, however, that its contribution has to be fairly small.

We have shown that a rather large molecule as C\textsubscript{3}F\textsubscript{6} has, in low fluence irradiation conditions, a multiphoton dissociation behaviour similar to that of smaller molecules. Further experimental work is needed to check whether the general features that the smaller molecules show in multiphoton absorption can be extended for any molecular size by suitably choosing the irradiation conditions, or it is a particular behaviour of perfluoropropene.

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