Spectrochimica Acta, Vol. 46A, No. 4, pp. 455 – 458, 1990.
Printed in Great Britain.

0584 – 8539/90 $3.00 + 0.00

Multiphoton Dissociation of C_3F_6 and CF_2HCl

M. Santos, C. Sigüenza, J.A. Torresano and P.F. González-Diaz.

Instituto de Optica "Daza de Valdés" C.S.I.C.
Serrano 121, 28006 MADRID (SPAIN)

Abstract- Multiphoton dissociation experiments in perfluoropropene and difluorochloromethane have been carried out with one or two wavelengths. It is shown that the increase of selectivity induced by a nonresonant radiation is attributable to an enlagement of the unimolecular reaction regime. The behaviour of large and small molecules when irradiated with two IR laser beams is different. Whereas the distinguishability between unimolecular and collisional regimes is enhanced for sufficiently large molecules, it tends to be smoothed in the case of small molecules.

INTRODUCTION

AMONG the processes involving interaction of laser light with matter, multiphoton absorption and dissociation of polyatomic molecules by strong IR fields has attracted great attention in recent years [1].

The two frequencies technique, in which the molecules are irradiated at two different wavelengths, allows a significant increase of both the selectivity and the yield of the dissociation process. Therefore, this technique has been used in isotope separation [1,2]. As the additional nonresonant wavelength is thought to act upon upper boundary of the discrete level pattern, beyond which the levels are very densely packed forming the so-called quasicontinuum, the two frequencies method can be used to discriminate between these two regions.

In particular, the bottleneck effect [1] that tends to inhibit excitation through higher energy levels may be deactivated by the nonresonant radiation. This would, in turn, induce a population decrease in the upper discrete levels before reaching the quasicontinuum, and drive the process to completion.

It may be thought that the effective size of a molecule with respect to multiphoton dissociation could characterize the extent at which the discrete levels contribute to this process. So, "small" molecules contribute with a larger number of well defined discrete levels to multiphoton dissociation than large molecules which would thereby dissociate under less stringent irradiation conditions.

As a consequence, and relative to the dissociation process itself, irradiation of a molecule with two different wavelengths may in some sense induce a given "change" in its effective size.

The aim of this work is to compare the results obtained by using infrared radiation at one and two wavelengths for two differently sized molecules: perfluoropropene (C_3F_6) and difluorochloromethane (CF_2HCl). Multiphoton dissociation of C_3F_6 driven by a single wavelength has been studied by NIP et al [3] and by SANTOS et al [4]. It was established that this molecule behaves as a rather "large" molecule in the sense above alluded and that its most probable multiphoton reaction pathway is:

$$C_3F_6 \xrightarrow{nh\nu} C_2F_4 + CF_2:$$
$$2CF_2: \rightarrow C_2F_4$$

At higher pressures, besides C_2F_4 some amount of C_2F_6 is also present among the products. Unimolecular dissociation of CF_2HCl induced by a single wavelength has been extensively studied by many authors [5,6]. This molecule seems to behave as a "small" molecule with respect to multiphoton dissociation along the pathway

$$CF_2HCl \xrightarrow{nh\nu} CF_2: + HCl$$

No product other than C_2F_4 has been detected in this reaction.

EXPERIMENTAL

The experimental arrangement we have used is schematically given in Fig. 1. NaCl lenses of different focal lengths were inserted to vary the fluence, F, at the cell position. Two pulsed TEA CO_2 lasers (Lumonics 101 and 103) have been used as radiation sources. With a typical CO_2 gas mixture, pulse shapes consisted of a ≈80 ns peak followed by a tail of about 1µs. Carefully setting the spark gap pressure and lasing line it was checked by a photon drag detector (Rofin, Model 7415) that both lasers where fired within 500 ns-1 µs of each other.

The experiments were carried out at room temperature in a pyrex cell 9.5 cm long with a total volume of ≃71 cm^3, which was equipped with NaCl end windows. In all the cases samples were irradiated with 50 laser shots.

A pyroelectric detector (20D-Lumonics) was employed to measure the incident pulse energy. Attenuation of the incident energy was accomplished by inserting in the optical lines CaF_2 plates and/ or polythene films.

Dissociation yield measurements were carried out on the final products by infrared absorption spectroscopy (we used a Perkin Elmer 599B spectrophotometer).

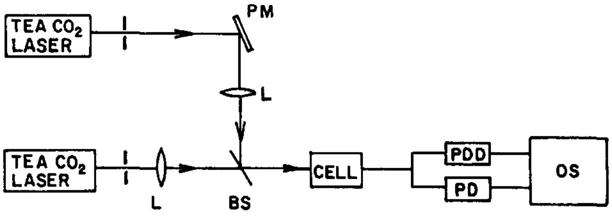

Fig. 1. Experimental setup for two frequencies experiments. PM: plane copper mirror; L: NaCl lenses; BS: beam splitter; PDD: photon drag detector; PD: pyroelectric detector; OS: oscilloscope.

Perfluoropropene (C_3F_6) gas sample supplied by Prof. H. van den Bergh, and commercial difluorochloromethane (CF_2HCl) (Matheson 99.9 %) were used without further purification.

RESULTS AND DISCUSSION

Perfluoropropene- The laser line at 9.603 μm coincides with the linear absorption maximum of the C-F stretching vibration of the central carbon atom in the C_3F_6 molecule [7] and has been used to preheat the molecule vibrationally. The second laser line was varied over the laser spectrum with some gaps between bands.

The fluences F_1 and F_2 (which correspond to resonant and non-resonant radiation, respectively) have been chosen in such way that no dissociation is observed separately by using infrared spectroscopy.

In Fig. 2 we give the infrared spectra of C_3F_6 (a) before and (b) after dissociation. In spectrum (b) we can observe a significant proportion of C_2F_4 and C_2F_6. These molecules were identified respectively by absorptions at 1388, 1326, 1190 and 1182 cm^{-1}, and 1245 cm^{-1}. Analysis on the final products were carried out using the C_3F_6 band at 1033 cm^{-1}.

Fig. 3 represents the dependence of the fraction of molecules dissociated per laser pulse (f) on the wavelength of the additional dissociating beam (λ_2), while the wavelength of the exciting beam (λ_1) was kept fixed (λ_1=9.603 μm,P(26) line). It can be seen that the energy is more effectively deposited by the second laser at frequencies shifted to the red with respect to the linear maximum. F_1 was 0.75 Jcm^{-2} and each point was obtained at the maximum energy available from the second laser, E_2. From these curves we chose λ_2=10.148 μm for all other experiments.

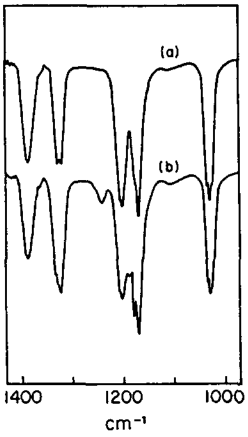

Fig. 2. IR spectrum of C_3F_6(a,b) before and after irradiation with a beam of wavelength λ =9.603 μm and fluence F=2.5 Jcm^{-2}.

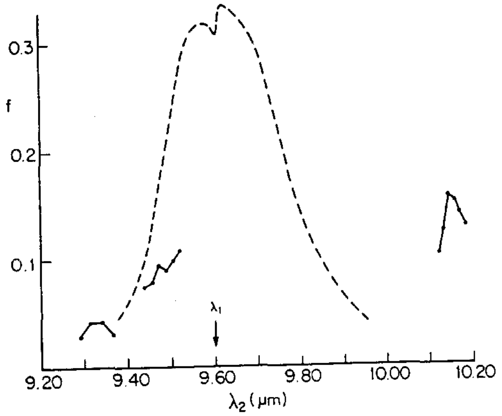

Fig. 3. Fraction f of C_3F_6 molecules versus non-resonant wavelength (λ_2). The resonant wavelength was kept constant at λ_1 = 9.603 μm. Dashed line represents the linear IR spectrum; p=2mb.

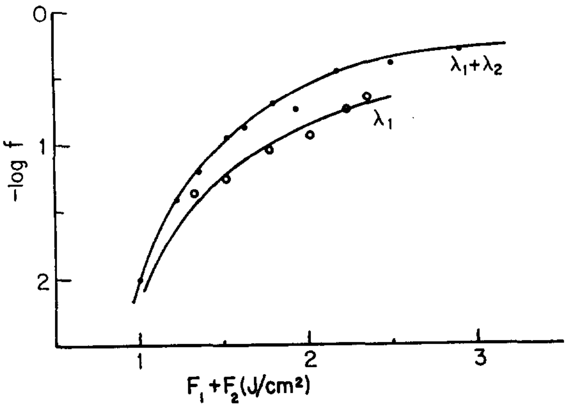

Fig. 4. (•) Fraction f of C_3F_6 molecules versus F_1 + F_2. (○) Fraction f of C_3F_6 molecules for a single wavelength experiment. In both cases p = 2mb, λ_1=9.603 μm and λ_2 = 10.148 μm.

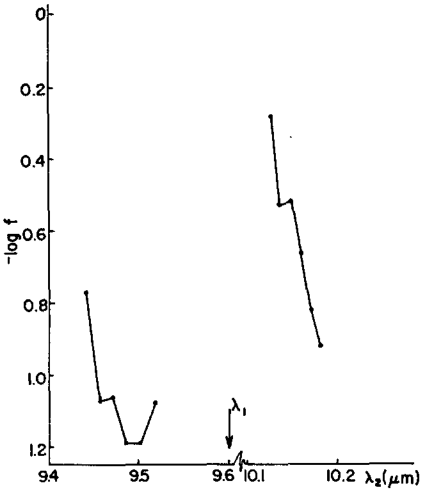

Fig. 5. Fraction f of C_3F_6 molecules versus the nonresonant wavelength λ_2 for constant fluence $F_1 + F_2$ Jcm^{-2}. $\lambda_1 = 9.603$ μm and p = 2 mb.

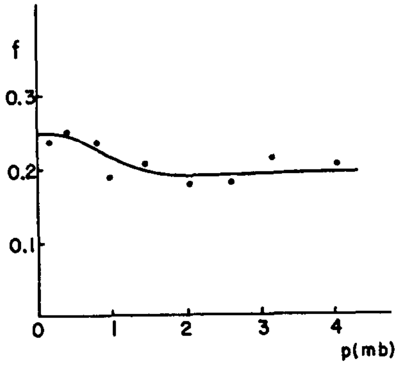

Fig. 6. Fraction f versus initial C_3F_6 pressure. $F_1 = 0.6$ Jcm^{-2}, $F_2 = 1.6 Jcm^{-2}$, $\lambda_1 = 9.603$ μm and $\lambda_2 = 10.148$ μm.

We have confirmed the increase in the dissociation yield of C_3F_6 by using two infrared wavelengths, as can be seen in Fig. 4, where we plot the dependence of the fraction f on the sum of the fluences of both lasers, $F_1 + F_2$; F_1 was kept constant at 0.6 Jcm^{-2}. The dependence of f on fluence is also sketched for the single wavelength case at the same pressure.

From the two curves of Fig. 4 and the data of Fig. 3 we have been able to interpolate the fraction of molecules dissociated per pulse at a fixed value of $F_1 + F_2 = 2$ Jcm^{-2}. The results are given in Fig. 5 where it can be checked that for $\lambda_2 > 10.12$ μm the dissociation yield decreases rather steeply with λ_2, whereas for $\lambda_2 < 9.52$ μm, there is a yield maximum.

Fig. 6 gives the fraction f versus the C_3F_6 pressure at fluences given in the figure . For the single wavelength case we obtained [4] that f is independent of perfluoropropene pressure within a pressure interval of 0-2.5 mb, so that the unimolecular and collisional regimes are indistinguisable. An increase in f for small values of pressure (range 0-0.8 mb), as that is observed in Fig. 6, indicates that the two wavelengths technique allows us to distinguish in this molecule between these two regimes. Even, it appears that this technique makes more effective the deposition of energy in the unimolecular regime than in the collisional one.

Difluorochloromethane- Fig. 7 shows the infrared spectra of CF_2HCl (a) before and (b) after laser irradiation. Analysis on the final products were carried out using the CF_2HCl band at 1113 cm^{-1}.

The laser line R(34) at 9.201 μm was used as the resonant wavelength. The same setup as in the experiments with C_3F_6 (Fig. 1) has been used in measurements carried out on CF_2HCl.

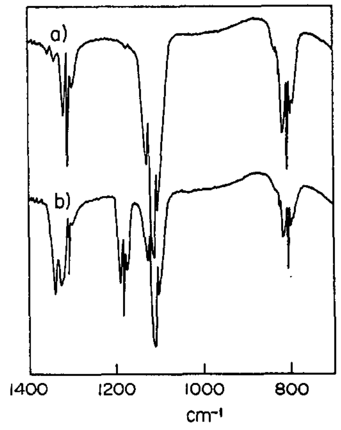

Fig. 7. IR spectra of CF_2HCl (a) before and (b) after irradiation with a beam of wavelength $\lambda = 9.201$ μm and F = 2.5 Jcm^{-2}.

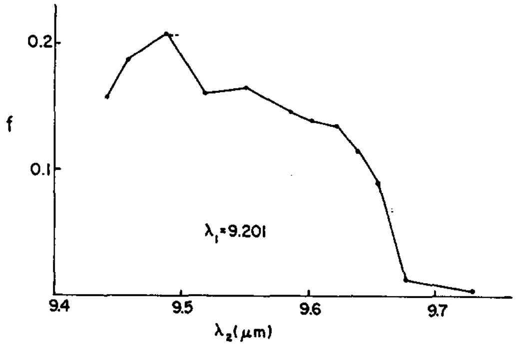

Fig. 8. Fraction f of CF_2HCl molecules versus nonresonant wavelength (λ_2). The resonant wavelength was kept constant at $\lambda_1 = 9.201$ μm, p = 3 mb.

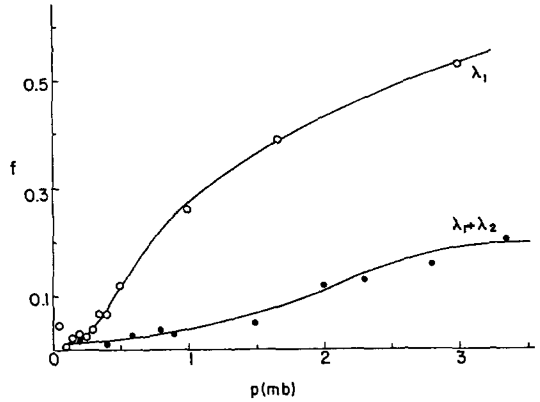

Fig. 9. Fraction f versus CF_2HCl pressure for one and two wavelength experiments. (○) $F_1 = 0.6$ Jcm^{-2}, $F_2 = 1.5$ Jcm^{-2}, $\lambda_1 = 9.201$ μm and $\lambda_2 = 9.488$ μm.; (•) $F = 2.1$ Jcm^{-2}, $\lambda = 9.201$ μm.

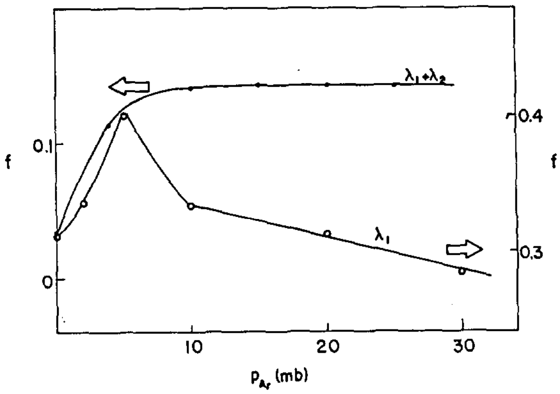

Fig. 10. Fraction f of CF_2HCl as a function of of the inert gas pressure for single and double wavelength experiments.

Fig. 8 shows the dependence of the fraction f on the wavelength λ_2. Consistent with the plot in this figure, we have chosen the line P(12) at 9.488 μm, inducing the largest yield, as the dissociating line. The fluence of the exciting line at 9.201 μm was kept constant at $F_1 = 0.6$ Jcm^{-2}.

In order to investigate the effect of a second nonresonant wavelength on the discrete level quasicontinuum transition, we have performed experiments in which the CF_2HCl pressure was varied along the range 0 - 3 mb for both the single and double wavelength cases. Results are displayed in Fig. 9. It can be observed that, quite the opposite to the C_3F_6 case, the second nonresonant radiation driving CF_2HCl molecules makes less distinguishable the dissociation unimolecular regime from the collisional one. This may be conventionally interpreted in terms of an increase of the selectivity of the dissociation process. According to Fig. 9, such an increase is atributable to an enlargement of unimolecular regime at the expenses of the collisional one. Unlike collisions which increase the effectiveness of the process by depopulating the bottleneck boundary downward, the additional nonresonant wavelength seems to depopulate the boundary upward, driving the molecules through a "shorter" quasicontinuum to dissociation. It is in this sense that we might talk about a "change" of the molecular size.

The increase of selectivity due to the activation of a second nonresonant wavelength may be better illustrated by adding an inert gas. Fig. 10 compares the effects produced by adding argon in the dissociation yield of single and double wavelengths induced photofragmentation of CF_2HCl. It is clearly observed that, whereas the fraction f has an abrupt maximum at 5 mb of added argon for the single wavelength plot, at least in the studied range, the dissociation yield in the double wavelength curve reaches a maximum at which it saturates, indicating so that the nonresonant radiation tends to inhibit the dissociation poissoning effect of collisions [8] at large pressures of the inert gas

Acknowledgements- The authors wish to acknowledge Prof. H. van den Bergh of the Polytechnic University of Lausane for supplying the C_3F_6 sample. We want to thank Prof. P. A. Hackett from the National Research Council of Canada, for his helpful suggestions, and to A. Pino for technical help.

REFERENCES

[1] C.D. CANTRELL ed., Multiple-Photon Excitation and Dissociation of Polyatomic Molecules (Springer, Berlin) 1986).
[2] R.V. AMBARTZUMIAN and V.S. LETOKHOV, in: Chemical and Biochemical applications of lasers, Vol. **3**, ed. C.B. Moore (Academic Press, New York, 1977).
[3] V.S. NIP, M. DROUIN, P.A. HACKETT and C. WILLIS: J. Phys. Chem. **84**, 932 (1980).
[4] M.SANTOS, C. SIGÜENZA and P.F. GONZALEZ-DIAZ: Opt. Pur. Apl. **21**, 29 (1988).
[5] R. DUPERREX and H. VAN DEN BERGH: Chem. Phys. **40**, 275 (1979).
[6] J.C. STEPHENSON and S. KING: J. Chem. Phys. **69**, 1485 (1978).
[7] J.R. NIELSON, H.H. CLAASSEN and D.C. SMITH: J. Chem. Phys. **20**, 1916 (1952).
[8] R. DUPERREX and H. Van den bergh: J. Chem. Phys. **71**, 3613 (1979).