J. Phys. Chem. A **1997,** *101,* 2221−2228

ARTICLES

One- and Two-Color Infrared Multiphoton Dissociation of C_3F_6

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Received: May 21, 1996; In Final Form: January 3, 1997[⊗]

Multiphoton dissociation of C_3F_6 induced by one and two infrared laser beams is studied. The contribution of the different collisional processes to the yield is quantified using the recently extended McRae et al. model. It has been shown that the increase of the fluence in single irradiation and the change to the red of the second infrared pulse in double-beam experiments can have equivalent effects on the dissociation. These effects are an important increment in the yield and the extinction of the influence of the homogeneous collisions between C_3F_6 molecules on the process. In double-irradiation experiments, the introduction of time delays between the two laser pulses also leads to large enhancements of the dissociation, giving rise to two yield maxima when the delays are around 2 and 65 μs. A change in the final proportion of the dissociation products induced by modifying the frequency of the second pulse has been detected in the double-irradiation experiments.

1. Introduction

Irradiation of a molecule by two (or in general, several) infrared (IR) beams[1−4] is a technique that is often employed in multiphoton dissociation (MPD) studies. This method allows a better understanding of the process, introducing new experimental variables such as the fluence and the frequency of the second beam and the time delay between both laser fields. The first pulse, nearly resonant with an IR fundamental absorption band of the parent compound, excites the molecules through the low-lying discrete levels. The second beam, usually fixed to a red-shifted wavelength with respect to the former to account for the anharmonicity, drives the absorption through the higher discrete levels and the quasicontinuum until the dissociation limit is overcome. Therefore, by using this dichromatic double irradiation, the bottleneck effects that prevent the multiphoton excitation can be circumvented, and a dissociation yield larger than in single-irradiation experiments is usually obtained. In these experiments, it can be considered that a change in the effective size of the molecule in relation to the MPD process[5] is induced; that is, the *strength* of the anharmonic barrier is modified. We have defined[6] the anharmonic barrier as the ensemble of all quantum characteristics of a molecule that inhibit the multiphoton absorption process. It consists of two main components: (a) the vibrational barrier, originated by the progressive anharmonic detuning of the absorption of the infrared photons, initially resonant with the first vibrational transition; (b) the rotational barrier, originated by the existence of the rotational selection rules, which prevents a large proportion of molecules from interacting with the radiation field.

Intermolecular energy transfers induced by collisions also modify the strength of the anharmonic barrier: A mechanism that increases the extent of the molecular excitation by reducing the rotational barrier consists in replenishing of laser-induced rotational hole burning through translational to rotational energy transfer, T−R (rotational hole filling[7]). Another mechanism that lowers the vibrational barrier is the overcoming of the anharmonic bottleneck through V−V′ energy transfer.[8] These two processes are effective only if the collisions take place in the presence of IR photons. Other collisional mechanisms, acting both during and after the laser pulse, are vibrational energy pooling,[9] which takes place when two molecules in the quasicontinuum collide, resulting in one highly excited partner being capable of dissociation, and collisional induced vibrational quenching of excited molecules through vibrational to translational energy transfer[1] (V−T).

Recently,[6] we have extended the method previously developed by McRae et al.[10−12] for the analysis of the contribution of the different collisional processes to IR multiphoton dissociation. Our extension allows the distinction, in the collisional sequence corresponding to one homogeneous collision, of those processes that affect the dissociation yield and that need the presence of IR photons to be effective (e.g., overcoming of the anharmonic bottleneck) from those that have not this requirement (e.g., vibrational energy pooling).

Multiphoton dissociation of C_3F_6 was first studied by Nip et al.,[13] who proposed the following dissociation reaction

$$C_3F_6 + nh\nu \rightarrow C_2F_4 + CF_2 \tag{1}$$

where recombination reactions between the formed CF_2 radicals give rise to the formation of more C_2F_4 and, in a minor proportion, to C_2F_6. We have found[14] another product, poly(tetrafluoroethylene), $(CF_2)_n$, which under certain conditions could represent up to 30% of the dissociated C_3F_6. We have also shown that the strength of the anharmonic barrier for this molecule is strongly dependent on the irradiation fluence. As a consequence, the contribution of the different collisional mechanisms to the absorption and dissociation processes is also largely modified by the pulse fluence. This behavior suggests that C_3F_6 could be a suitable system to be investigated with the extended analysis method cited above.

In this paper, we study and quantify the contribution of the different collisional mechanisms to the multiphoton dissociation process of C_3F_6, induced by single (MPD) and double (MPD2) infrared laser irradiation, using the extended McRae analysis

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

S1089-5639(96)01454-5 CCC: $14.00

method. Although McRae et al. applied their method to two-color two-beam dissociation of 1-bromo-2-fluoroethane,[15] this is the first time that such a kind of method is applied to double-irradiation experiments with a variable temporal delay between the two laser beams. We have carried out these experiments with both beams tuned at the same or at different wavelengths. Hereafter, we will refer to these situations as monochromatic and dichromatic double irradiation, respectively. We also investigate the influence of the time delay introduced between the two laser fields on the process and the dependence of the dissociation and recombination reactions on the different irradiation parameters.

2. Experimental Section

Two TEA CO_2 lasers, Lumonics K-101 and K-103, were employed for the irradiation of the C_3F_6 samples. They were equipped with frontal Ge multimode optics (85% reflection for K-101 and 35% for K-103) and rear diffraction gratings with 135 lines/mm blazed at 10.6 μm. They were also equipped with low jitter trigger devices (Lumonics 524) which provided a jitter between the two pulses lower than 100 ns in the double-irradiation experiments. The lasers operated with a CO_2:N_2:He mixture in the proportion 8:8:84.

In single-irradiation experiments, we have used the CO_2 K-103 laser tuned at the 9P(26) line at 9.603 μm, which is nearly resonant with the C−F stretching mode of C_3F_6.[16] In the double-irradiation case, the frequency of the K-101 laser was fixed at the same 9P(26) laser line and provided the leading pulse in delayed experiments. We employed the pulse originated in the K-103 laser as the second IR field. Its frequency was also tuned at the 9P(26) line in the experiments of monochromatic double irradiation, while in the dichromatic case it was fixed at the 10R(36) line at 10.148 μm. This frequency corresponds to the maximum of the multiphoton dissociation spectrum obtained under double irradiation with the first pulse frequency fixed to 9.603 μm.[17]

Laser pulse temporal profiles were observed with a photon drag detector (Rofin Sinar 7080) and consisted of a spike (110 ns (fwhm) for K-101 and in the case of K-103, 65 ns for the 9P(26) line, and 140 ns for the 10R(36)), followed by a tail approximately 1.5 μs long in all cases. These temporal profiles were constant throughout the study.

Two cylindrical Pyrex cells, 8.8 and 9.5 cm long, 0.95 and 1.5 cm radius, and 30.5 and 71.0 cm^3 total volume, respectively, fitted with NaCl windows, contained the gas during the irradiation. The largest cell was only used in the single-irradiation experiments at a fluence of 6.8 J cm^{-2}. The laser beams were directed into the absorption cell in a near-parallel irradiation geometry in which the laser beams were slightly focused by 1.5 and 2 m focal length NaCl lenses.

In Figure 1, we show the experimental arrangement used in the double-irradiation experiments. The time delay between the two IR pulses was controlled by means of a digital delay generator, Berkeley Nucleonics BNC 7036A, which allows a delay between 0 and 100 μs with a step of 1 ns.

The laser fluence was calculated as the ratio of the pulse energy measured with a Lumonics 20D pyroelectric detector, and the "1/e" cross-sectional beam area was measured at the cell position with a pyroelectric detector array Delta Development Mark 4. (These beam areas, also used for computing the irradiation volumes, V_I's, are given in the captions of Figures 2 and 3). The laser energy was changed by placing CaF_2 plates in the optical paths and controlling on the high-voltage settings of the lasers for a finer adjust. The estimated uncertainty in the absolute values of the fluence was around 8% (5% being a constant error coming from the nominal detector calibration factor).

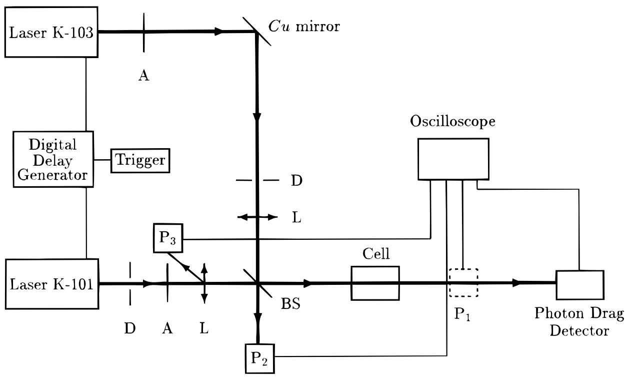

Figure 1. Experimental setup used in double-irradiation experiments: A, CaF_2 attenuators; D, diaphragms; BS, Ge beam splitter; L, NaCl lenses; P_i, pyroelectric detectors.

Perfluoropropene gas samples (99.0%) were kindly provided by Prof. H. van der Bergh (Ecole Polytechnique Fédérale de Lausanne, Switzerland) and used without further purification. Sample pressures in the cell were measured with two (0−1 and 0−10 mbar) MKS Baratron gauges. The dissociation yield was determined by monitoring the change in the absorbance of the 1036 cm^{-1} C_3F_6 band,[16] with a FTIR spectrophotometer (Perkin-Elmer Model 1725X). To study the influence of the different experimental variables on the dissociation reaction, we have used the two dimensionless parameters

$$\delta_1 = \frac{[C_2F_4]}{1.5\Delta[C_3F_6]} \tag{2}$$

$$\delta_2 = \frac{[C_2F_6]}{\Delta[C_3F_6]} \tag{3}$$

where $\Delta[C_3F_6]$ is the change in the concentration of hexafluoropropene due to dissociation.

According to eq 1, $\delta_1 = 1$ would mean that all the formed CF_2 radicals would be transformed into C_2F_4. The produced amounts of C_2F_4 and C_2F_6 were determined by FTIR spectroscopy, using measurements of their absorption bands at 1189 and 1250 cm^{-1}, respectively.[18,19]

3. Results and Discussion

In the method proposed by McRae et al. for the analysis of the contribution of the different collisional mechanisms to the dissociation process,[10] the number of parent molecules, N_n, left in the cell after n irradiation pulses is given by

$$N_n = N_0 \prod_{k=1}^{n} [1 - (V_I/V_c) f_k(\phi_k, \alpha_{k-1}, \beta_{k-1})] \tag{4}$$

where N_0 is the initial number of parent molecules, V_I and V_c are the irradiation and the total cell volumes, and $f(\phi,\alpha,\beta)$ is the single-pulse decomposition probability. This is a function of the fluence, ϕ, and the partial pressures of parent molecule, α, and dissociation products or any other buffer gas, β.

They assume a power dependence of f, on the partial pressures in the cell given by

$$f(\phi,\alpha,\beta) = \sum_{i=1} \sum_{j=0} h_{ij}(\phi) \alpha^{i-1} \beta^{j} \tag{5}$$

where the coefficients h_{ij} depend only on the irradiation fluence (ϕ).

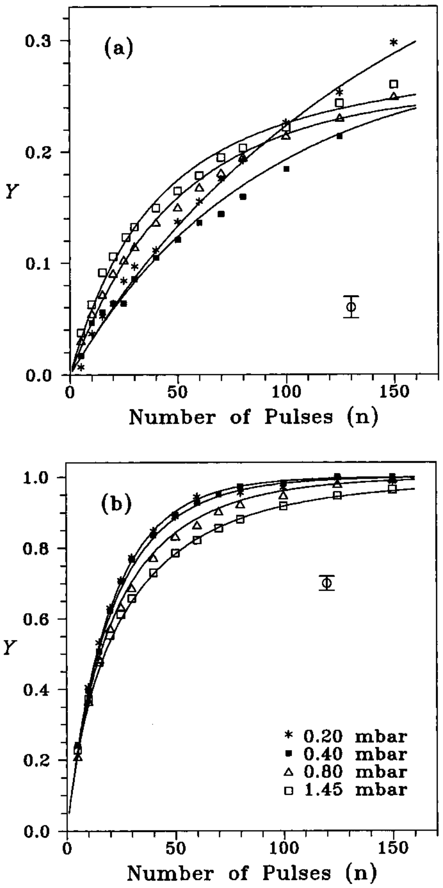

Figure 2. Fraction of dissociated C_3F_6 molecules, Y, versus the number of laser pulses for different values of the initial pressure. Solid lines represent the fits of the experimental points to the extended method described in the text (section 3). (a) The irradiation fluence was $\phi = 2.3$ J cm^{-2}, and the beam area was 0.32 ± 0.01 cm^2. (b) $\phi = 6.8$ J cm^{-2}, and a beam area of 0.54 ± 0.01 cm^2.

This method takes into account the variations in the pulse-to-pulse yield induced by the change of the reactant and product partial pressures during the course of the experiment. The magnitude and sign of the parameters h_{ij} provide information about the contribution to the dissociation coming from the different collisional sequences. Our modification to the method[6] consists basically in the introduction of an initial parent pressure dependence in the parameter corresponding to one homogeneous collision, h_{20}. This dependence is of the form

$$h_{20} = \begin{cases} h_{20}^{a}, & \text{if } P < P' \\ h_{20}^{a} + m(P - P'), & \text{if } P' < P < P'' \\ h_{20}^{a} + h_{20}^{b}, & \text{if } P > P'' \end{cases} \qquad (6)$$

The parameter h_{20}^{a} is associated with those processes taking place independently of the presence of the laser field, that is, energy pooling and quenching, while h_{20}^{b} is related to those operating only in the presence of infrared photons. Thus, h_{20}^{b} can be interpreted as a measurement of the maximum weakening that can be induced in the anharmonic barrier by means of homogeneous collisions at some given irradiation conditions. The sign of h_{20}^{a} is determined by the competition between energy pooling and vibrational quenching, being positive if the former dominates and negative otherwise. The parameter h_{20}^{b} is always positive. P' and P'' are respectively the initial pressure of the parent molecule at which the collisional processes associated with h_{20}^{b} begin to be active and that at which they saturate. The rate at which this saturation value is reached is given by the slope m. The value of P' corresponds to the pressure at which the number of collisions taking place in the time of the pulse becomes large enough to start the deactivation of the anharmonic barrier.

In the application of the extended McRae method to the MPD of the C_3F_6 molecule, we have splitted the term corresponding to one single heterogeneous collision to separate the contribution due to collisions between the parent molecule and the two gaseous products C_2F_4 and C_2F_6. These terms are written as

$$h_{11}(\mathrm{X})\, S(\mathrm{X})(C_0 - C_n) \qquad (7)$$

where X represents either C_2F_4 or C_2F_6. C_n is concentration of C_3F_6 in the reaction cell after n IR pulses, C_0 being the initial value. The parameters S(X) are the number of C_2F_4 or C_2F_6 molecules that are produced from a dissociated molecule of C_3F_6 and are directly determined from the measured values of δ_1 and δ_2 (eqs 2 and 3): $S(C_2F_4) = 1.5\delta_1$ and $S(C_2F_6) = \delta_2$.

The inclusion of other parameters that represent processes involving more than one molecular collision has not been necessary in any of the fits of the experimental data.

Single Irradiation. We have used the fraction of C_3F_6 molecules dissociated per laser pulse in the whole cell, given by

$$Y = 1 - N_n/N_0 \qquad (8)$$

for quantifying the dissociation yield.

In Figure 2, we give the variation of the yield Y versus the number of laser pulses, n, for two different values of the laser fluence. The calculated yields obtained by applying the method outlined at the beginning of this section appear as continuous lines in the figure. In the fits, each experimental point has been weighted by the inverse square of the associated error. Table 1 shows the relevant parameters obtained from the fits together with their standard deviations, the chi-square[20] (χ^2) and the number of degrees of freedom (ν). For the higher fluence value, 6.8 J cm^{-2} (Figure 2b), a good fit is obtained by taking into account just the collisionless dissociation, h_{10}, and the heterogeneous collisions C_3F_6–C_2F_4 and C_3F_6–C_2F_6 represented by the parameters $h_{11}(C_2F_4)$ and $h_{11}(C_2F_6)$, respectively. The opposite signs of both parameters imply that, while the collisions of C_3F_6 with C_2F_4 inhibit the dissociation process, those with C_2F_6 are favorable to it. A possible explanation to this could be the existence of an absorption band at 1025 cm^{-1} (16 cm^{-1} to the red of the laser frequency) in the C_2F_6 spectrum,[19] which would allow this compound to act as a "sensitizer",[10,21] by absorbing energy from the IR field and transferring it to the C_3F_6 molecule in the collision, through V–V′ exchange. The absence of the h_{20} parameter in the final fits means that, at these fluence conditions, homogeneous collisions between C_3F_6 molecules do not play an important role in the MPD process, in agreement with the existence of the weak anharmonic bottleneck already detected in this molecule[14] and suggesting a low influence of the V–V′ energy transfer process between parent molecules excited in the quasicontinuum. It is also worth noting the high value obtained for the collisionless parameter h_{10}. This means that a large part of the irradiated molecules breaks without collisional assistance in accordance, not only with the presence of a small anharmonic barrier but also with the observed trend of the dissociation probability at the low initial C_3F_6 concentration limit.[14]

When the fluence is fixed to 2.3 J cm^{-2}, the analysis method provides a different picture of the MPD process. The role of heterogeneous collisions does not change with respect to that obtained for the highest fluence. However, in this case, we

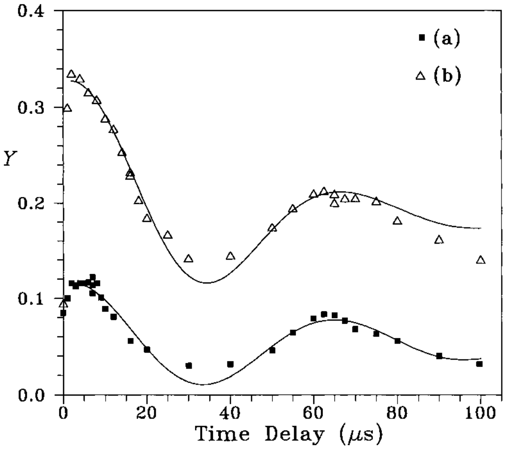

Figure 3. Dependence of the fraction of dissociated molecules, Y, on the time delay, $\Delta\tau$, between the two laser fields. The initial C_3F_6 pressure was $P_0 = 0.9$ mbar, and 50 pairs of laser pulses were used. In each pair, the wavelength, fluence, and beam area of the first pulse were kept constant to $\lambda_1 = 9.603$ μm, $\phi_1 = 0.8 \pm 0.1$ J cm^{-2}, and $A_1 = 0.38 \pm 0.01$ cm^2, respectively. (a) Monochromatic irradiation, $\lambda_2 = \lambda_1$, $\phi_2 = 1.2 \pm 0.1$ J cm^{-2}, and $A_2 = 0.32 \pm 0.01$ cm^2. (b) Dichromatic irradiation, $\lambda_2 = 10.148$ μm, $\phi_2 = 1.6 \pm 0.2$ J cm^{-2}, and $A_2 = 0.25 \pm 0.01$ cm^2.

TABLE 1: Model Parameters and Their Standard Deviations Obtained for the Fits Corresponding to the Experiments of Figure 2[a]

parameter	Figure 2a ($\phi = 2.3$ J cm^{-2})	Figure 2b ($\phi = 6.8$ J cm^{-2})
h_{10}	0.035 ± 0.001	0.72 ± 0.01
$h_{11}(C_2F_4)$	-0.35 ± 0.06	-1.2 ± 0.2
$h_{11}(C_2F_6)$	0.85 ± 0.30	3.5 ± 0.9
h^b_{20}	0.025 ± 0.002	
P'	0.35 ± 0.07	
P''	0.8 ± 0.2	
m	0.066 ± 0.015	
ν	48	52
χ^2	37	55

[a] P'' has been computed from the values of h^b_{20}, P', and m through eq 5. Units are mbar for P' and P'', mbar^{-1} for $h_{11}(C_2F_4)$, $h_{11}(C_2F_6)$, and h^b_{20}, and mbar^{-2} for m. The chi-square (χ^2) and the number of degrees of freedom (ν) of each fit are also given.

have to take into account the homogeneous collisions that take place during the laser pulse. They induce a weakening of the anharmonic barrier and produce an increment in the dissociation yield as it is indicated by the positive sign of h^b_{20}. On the other hand, it is not necessary to include the parameter h^a_{20} in the fits, confirming in this way that collisions between C_3F_6 molecules excited in the quasicontinuum do not contribute to the MPD process. In addition, a study of the MPD of C_3F_6 carried out in the presence of argon[22] strongly suggests that the nature of the anharmonic barrier in C_3F_6 is essentially vibrational.

The value of the pressure P' enables us to calculate the minimum number of collisions in the time of the pulse that are required to weaken effectively the anharmonic barrier. If we suppose that the mean molecular speed is the given by the kinetic theory and we take a collisional cross section[23] $\sigma = 1.1 \times 10^{-14}$ cm^2, we obtain the number of collisions to be approximately two, for an effective temporal pulse width around 500 ns. The obtained value of P' is close to the pressure found in our previous work,[14] 0.3 mbar, which corresponds to the minimum of the dissociation yield versus the initial pressure of C_3F_6. The saturation value of h_{20} (equal in this case to h^b_{20}) is reached for an initial C_3F_6 pressure $P'' = 0.8$ mbar; at this pressure we obtain the largest deactivation of the bottleneck effect induced by homogeneous collisions.

The collisionless parameter h_{10} is around 20 times smaller than the one obtained for the higher fluence, $\phi = 6.8$ J cm^{-2}. Under similar experimental conditions, a change in the laser fluence from 2.6 to 5.9 J cm^{-2} gives rise to only a 4-fold increase in h_{10} in the MPD of CF_2HCl.[6] This difference supports the idea that the anharmonic barrier can be circumvented more easily in C_3F_6 than in CF_2HCl.

The dissociation products obtained for the experiments of Figure 2 are the same that were found previously[14] (i.e., C_2F_4, C_2F_6, and $(CF_2)_n$). For the two fluence values that we used, and for a given initial pressure, the parameters δ_1 and δ_2 defined in section 2 are nearly constant when the number of pulses is increased. For the highest pressures, we saw that $\delta_1 < 0.66$, which is, in principle, the minimum value expected from reaction 1 (corresponding to the situation in which the formed CF_2 radicals do not dimerize to C_2F_4). This result could mean that reaction 1 is not the only dissociation path in the MPD of C_3F_6, at least under high-pressure conditions, or that the directly formed C_2F_4 from C_3F_6 is involved in some recombination reactions.

Double Irradiation. The dependence of the MPD2 yield, Y, on the time delay between the two laser pulses, $\Delta\tau$, is shown in Figure 3 for monochromatic and dichromatic double irradiation. In both cases, a first maximum is obtained corresponding to a $\Delta\tau$ of a few microseconds. This maximum arises as a result of the competition between the different mechanisms favoring and inhibiting the dissociation process, such as V−V′ and V−T intermolecular energy transfer, and the diffusion of the molecules irradiated by the first pulse outside the volume irradiated by the second one. The finite temporal width of the laser pulse also contributes to the appearance of this maximum.

The second maximum appearing in both curves can be associated with the reflection of the energy wave originated by the V−T intermolecular energy transfer on the cell walls. Similar experiments carried out in $CFHCl_2$ with cells of different diameter support this interpretation.[24] Together with this thermoacoustic wave, there may exist another wave associated with the V−V′ intermolecular transfer. This vibrothermal wave is reflected on the cell walls and returns to the central core, resulting in an overexcitation of the molecules therein. The value of $\Delta\tau$ for the second maximum, ≈65 μs, corresponds to the time at which this wave arrives to the central core simultaneously with the second IR field. For a given cell, this characteristic time only depends on the parameters defining the first IR pulse and on the nature of the molecule. In this sense, we can say that the second pulse acts like a "probe" beam of the situation created in the cell by the first one.

In Figure 3, the continuous lines represent the fits of the experimental points to a simple model that we have developed for the double-irradiation process,[24] which takes into account the existence of the thermoacoustic wave and relates the energy absorption from both beams with the effective size of the molecule.[5]

In Figures 4 and 5, we give the dependence of the dissociation yield, Y, on the initial C_3F_6 pressure in the cell, P_0, for two different delay values: $\Delta\tau = 0$ and $\Delta\tau = 3$ μs, respectively. Figures 4a and 5a correspond to monochromatic irradiation, whereas Figures 4b and 5b present the behavior for pulses of different frequencies.

The results for monochromatic irradiation suggest that the effect of the anharmonic barrier is relevant in this MPD2 process. For simultaneous irradiation and rather small initial C_3F_6 pressure, the number of homogeneous collisions that take

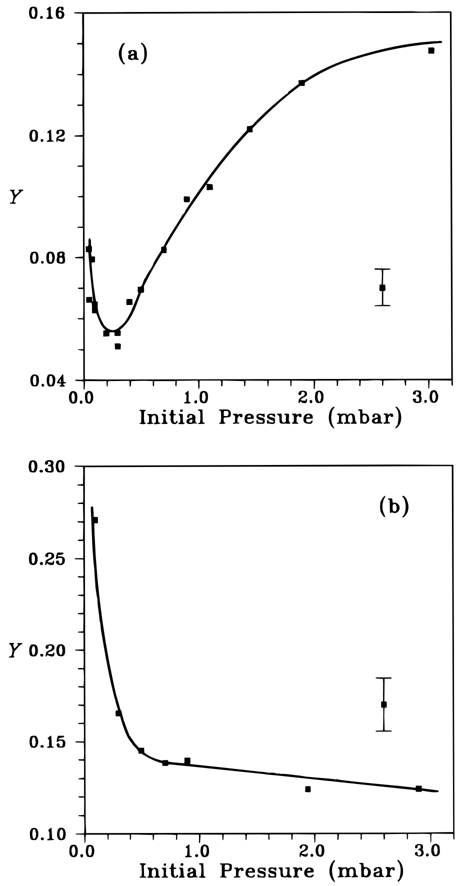

Figure 4. Dependence of the fraction of dissociated molecules, *Y*, after 50 pairs of simultaneous laser pulses on the initial C_3F_6 pressure in the cell: (a) monochromatic irradiation and (b) dichromatic irradiation. All other conditions as in Figure 3.

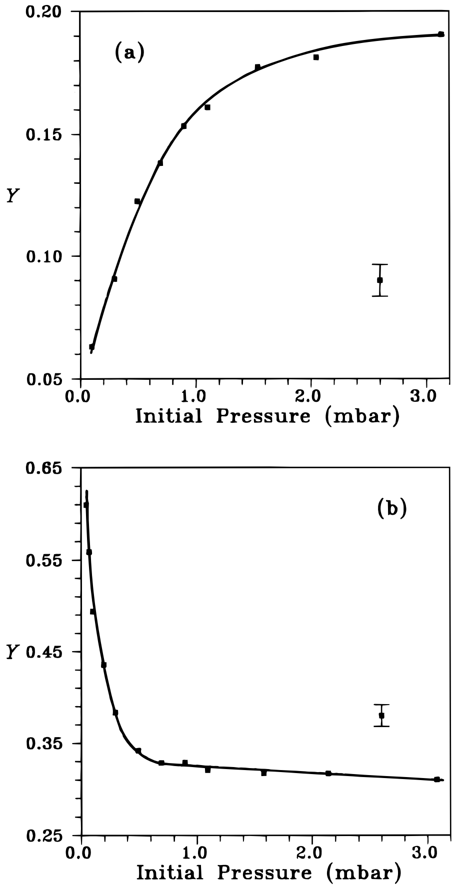

Figure 5. Same as in Figure 4 for a time delay, $\Delta\tau = 3\ \mu s$, between the two IR pulses.

TABLE 2: Model Parameters and Their Standard Deviations Obtained for the Fits Corresponding to the Experiments of Figure 6[a]

	monochromatic		dichromatic	
parameter	$\Delta\tau = 0\ \mu s$	$\Delta\tau = 3\ \mu s$	$\Delta\tau = 0\ \mu s$	$\Delta\tau = 3\ \mu s$
h_{10}	0.034 ± 0.001	0.030 ± 0.002	0.074 ± 0.001	0.284 ± 0.005
$h_{11}(C_2F_4)$	−0.51 ± 0.03	−0.46 ± 0.04	−0.38 ± 0.03	−1.89 ± 0.07
$h_{11}(C_2F_6)$	1.6 ± 0.1	1.4 ± 0.2	0.82 ± 0.15	6.4 ± 0.3
h_{20}^{b}	0.035 ± 0.001	0.047 ± 0.002		
P'	0	0		
P''	0.90 ± 0.05	0.52 ± 0.08		
m	0.039 ± 0.001	0.09 ± 0.01		
ν	50	49	51	53
χ^2	11	60	63	86

[a] P'' has been computed from the values of h_{20}^{b}, P' and m through eq 5. The chi-square (χ^2) and the number of degrees of freedom (ν) of each fit are also given. Units are the same indicated in Table 1.

place during the effective time of the pulses is not enough to induce the overcoming of the anharmonic barrier. The only relevant collisional processes are those inhibiting the dissociation through V−T and V−V′ intermolecular transfers, justifying the initial decrease of the yield as P_0 increases. As the C_3F_6 pressure grows, the number of homogeneous collisions also increases, and the mechanism of weakening of the anharmonic barrier becomes effective, giving rise to the increment in the yield as P_0 grows that is observed in Figure 4a. The curve "yield/P_0" found in the MPD study of C_3F_6[14] for a fluence of 2.4 J cm^{-2} is very much coincident with the one shown in Figure 4a, including the position of the yield minimum around 0.2 mbar. (This fluence is roughly the sum of the fluences of the two pulses used in MPD2.)

When a time delay is introduced between the two-equal frequency IR pulses, the number of homogeneous collisions suffered by a C_3F_6 molecule interacting with the first field before the arrival of the second is larger for a given value of P_0. This allows a proportion of initially bottlenecked molecules to overcome the barrier and thus to get a higher excitation level above the dissociation limit by absorbing photons from the second laser field. In this way, the molecular RRKM rate becomes faster, giving rise to the larger dissociation yield found in delayed irradiation with respect to the simultaneous case. This also explains the shift to lower pressure values in the position of the minimum of Figure 4a. This shift leads to the progressive reduction of the initial decreasing yield region, until it becomes unobservable for sufficient long delays, as it is observed in Figure 5a.

Substantial changes take place in the above scheme if the dissociation process is induced by dichromatic irradiation with a suitable value of the second IR wavelength. In this case, due to the red-shifted frequency, the molecules excited to the bottleneck region by the first pulse can absorb more efficiently the second nonresonant field, so that the effect of the anharmonic barrier is largely suppressed. In this way, the introduction of a time delay between the two pulses would not produce an increment of the proportion of molecules absorbing the second IR pulse. Nevertheless, such an increment actually occurs when a suitable short delay is established because, in this case, the molecules can absorb the largest part of the energy delivered by the first laser pulse and so get a higher excitation level before the arrival of the second one.[25] This time delay must be nearly coincident with the total temporal width of the first pulse. In our case, we see in Figure 3b that, for 1.5 μs (approximately the first pulse width), the maximum has been reached. Because of the inhibitory character to the excitation of the homo- and

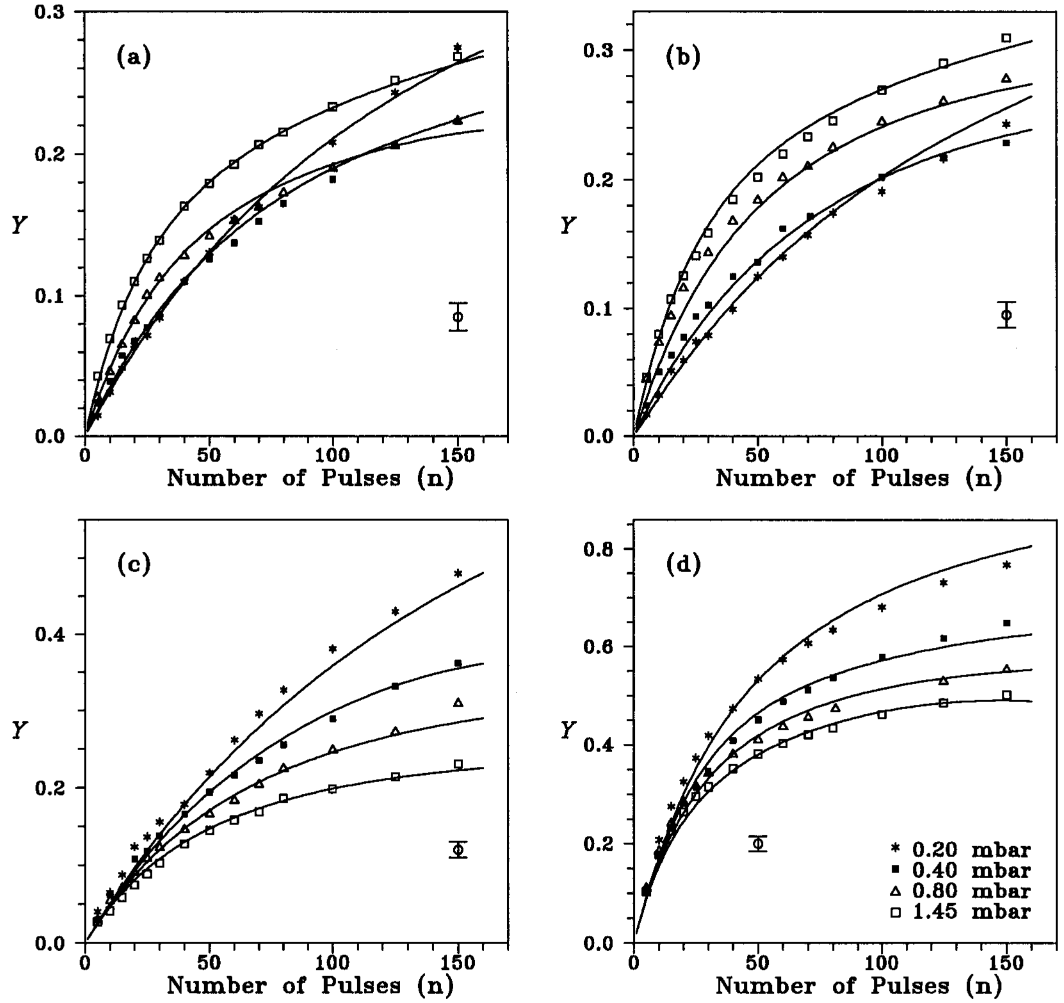

Figure 6. Fraction of dissociated C_3F_6 molecules, Y, versus the number of pairs of laser pulses for different values of the initial pressure: (a) monochromatic simultaneous irradiation, (b) monochromatic irradiation with a delay, $\Delta\tau$, of 3 μs between the two IR pulses, (c) dichromatic simultaneous irradiation, and (d) dichromatic irradiation and $\Delta\tau = 3$ μs. Solid lines represent the fits of the experimental points to the extended method described in the text. In each pair the wavelength and fluence of the first pulse were kept constant to $\lambda_1 = 9.603$ μm and $\phi_1 = 1.0 \pm 0.1$ J cm^{-2}. For mochromatic irradiation: $\lambda_2 = \lambda_1$ and $\phi_2 = 1.4 \pm 0.1$ J cm^{-2}. For dichromatic irradiation: $\lambda_2 = 10.148$ μm and $\phi_2 = 1.7 \pm 0.2$ J cm^{-2}. Other conditions as in Figure 3.

heterogeneous collisions, an increment in the value of the initial C_3F_6 pressure must induce a decrease of the yield for any value of the time delay, $\Delta\tau$, as is observed in Figures 4b and 5b. This situation is analogous to the one obtained in single irradiation for a fluence value of 6.8 J cm^{-2}.

The dissociation yield of C_3F_6 versus the number of pairs of laser pulses, n, is shown in the Figure 6a–d for monochromatic and dichromatic irradiation and for the two values of $\Delta\tau$ used in Figures 4 and 5. By applying the extended McRae model to the results of this figure, we can analyze the different dissociation schemes described above. In Table 2, we give the values of the relevant parameters and their associated standard deviations obtained in the fits. Note that, for delayed irradiation, the results obtained from the application of the method refer to the effect of the second infrared pulse, which acts on molecules affected by both the effect of the first laser and the time evolution during the established time delay. As can be expected for simultaneous monochromatic irradiation, the determined parameters are close to those obtained in single MPD for a fluence of 2.3 J cm^{-2}. The existence of a noticeable anharmonic barrier is supported by the small value of the collisionless parameter, h_{10}, and the dependence of h_{20} on the initial pressure of C_3F_6. In addition, the zero value obtained for the parameter h_{20}^a shows that there is no significant contribution to the dissociation yield coming from the energy pooling mechanism. Finally, we see that heterogeneous collisions have the same effect on the MPD2 process as in single MPD, i.e., inhibiting the dissociation in the C_3F_6–C_2F_4 case and enhancing it in the C_3F_6–C_2F_6 one.

The value of the limiting pressure P' is so small that the method cannot determine it with enough accuracy, and it has been set to zero in the fits. The difference of this situation with respect to the one obtained in single irradiation ($P' = 0.35$ mbar) is probably due to the larger effective temporal width of the pulse employed in MPD2 experiments.

The result of the fits obtained for $\Delta\tau = 3$ μs in monochromatic irradiation is also in accord with our previous discussion. The processes involved in the dissociation do not change with respect to the simultaneous case. The weakening of the anharmonic barrier is made clear in the higher value of m (h_{20}^b gets its maximum for a pressure $P'' = 0.5$ mbar, while this pressure is 0.9 mbar for $\Delta\tau = 0$).

The results for dichromatic irradiation resemble those obtained for single irradiation under high-fluence conditions. A large weakening of the anharmonic barrier, and therefore a substantial change in the dissociation process, is manifested in the obtained fit parameters: The homogeneous collisions do not have a noticeable influence on the dissociation, and only three parameters, those corresponding to the pressure-independent dissociation and the heterogeneous collisions, are sufficient to describe

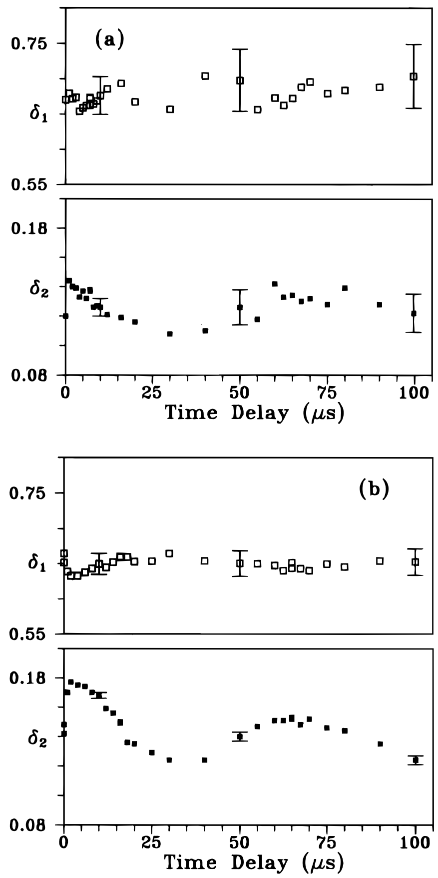

Figure 7. Proportions of C_2F_4 and C_2F_6 formed in the experiments of Figure 3, represented by the parameters δ_1 and δ_2 defined in the text: (a) monochromatic irradiation; (b) dichromatic irradiation.

the results. For simultaneous irradiation, the value of h_{10} is twice that found in the monochromatic case. When $\Delta\tau$ is fixed to 3 μs, the situation does not change qualitatively; however, the obtained yield is much larger than for $\Delta\tau = 0$, with a large increment in the pressure-independent contribution to the yield.

The dissociation products that we have obtained in the double-irradiation experiments of C_3F_6 are the same that we found for the single-irradiation case. The dependence of the parameters δ_1 and δ_2 on the time delay between the laser pulses is given in Figure 7 for the same experiments of Figure 3. We can see that the proportion of formed C_2F_6 is correlated with the obtained dissociation yield: The maxima (minima) of δ_2 are placed at those values of $\Delta\tau$ corresponding to the maxima (minima) of the yield, approximately. This clearly occurs for dichromatic irradiation and seems to appear in the monochromatic case as well. On the other hand, the proportion of formed C_2F_4 is nearly constant, within the limit of our experimental error.

For the experiments shown in Figures 4 and 5, we obtain that an increment in the C_3F_6 pressure, P_0, leads to a larger proportion of formed C_2F_6 and to a smaller proportion of C_2F_4, in agreement with the results obtained in single-irradiation experiments. Although both parameters tend to saturation, the limiting value of δ_1 remains constant as the wavelength associated with the second IR field changes, whereas δ_2 increases. This increment is small in the case of simultaneous irradiation and noticeable when the delay is 3 μs. In Figure 8, we show the dependence of δ_1 and δ_2 on P_0, for the delayed experiments.

These results suggest that, for some given values of $\Delta\tau$, P_0 and the wavelength of the second field, there exists a competition between the production of C_2F_6 and another product, different from C_2F_4, in the overall MPD2 process of C_3F_6. It seems reasonable to assume that this product is the polymer $(CF_2)_n$ that we have obtained in a significant amount because we have not detected any other dissociation product.

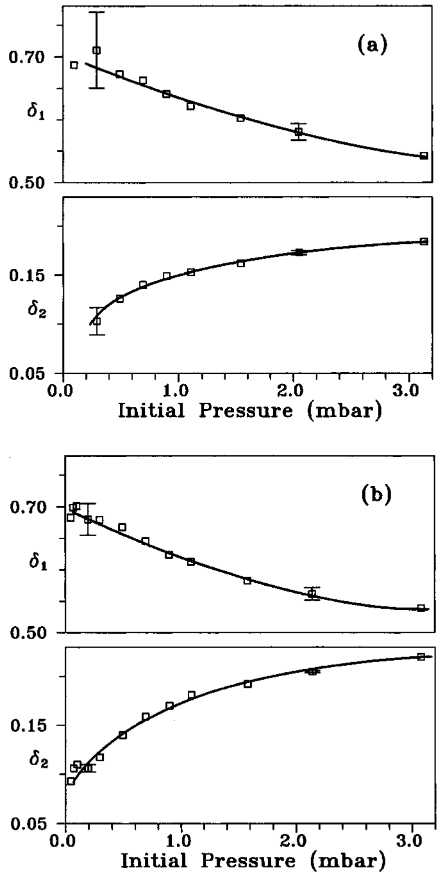

Figure 8. Same as in Figure 7 for the experiments of Figure 5.

The different energy content of the CF_2 radicals created in the dissociation of C_3F_6 could provide a possible explanation for this competition, if one admits that the less energetic CF_2's are more susceptible to engage in polymer formation. The larger amount of energy in the fragments formed by dichromatic irradiation is due to the weaker anharmonic barrier that C_3F_6 presents at these conditions with respect to the monochromatic case. In this way, the frequency of the second pulse would control the ratio between the production of polymer and C_2F_6 because it determines the energy content in the formed species.

4. Conclusions

In this work, we have analyzed and quantified the different collisional mechanisms involved in the infrared multiphoton dissociation of hexafluoropropene by using the extended McRae et al. method. For double-monochromatic irradiation, a rather small contribution from collisionless dissociation is found. We have established that homogeneous collisions play an important role in circumventing the bottleneck effect, but they do not give rise to any energy pooling transfer between the molecules excited in the quasicontinuum. These results are similar to those obtained from single-irradiation experiments at low fluence and support the existence of a significant anharmonic barrier in the MPD of C_3F_6 under these conditions. On the other hand, when the frequency of the second IR field is red-shifted with respect to that of the first pulse, the bottleneck effect is largely removed and leads to an important increase in the collisionless contribution to the process. In this case, the influence of homogeneous collisions disappears. The same conclusions are obtained from single-irradiation results at high fluences. In double-irradiation experiments, a time delay of a few microseconds between the two IR fields induces a large increment in the dissociation yield, giving rise to the occurrence of a maximum of the dissociation yield. For monochromatic irradiation, this effect is due to the large number of homogeneous collisions that take place before the arrival of the second pulse, weakening the strength of the anharmonic barrier. Nevertheless, for the dichromatic case, the yield increment is mainly due to the temporal distribution of the first pulse energy. In both cases, heterogeneous collisions between C_3F_6 and the two gaseous dissociation products have opposite effects: favoring the dissociation in the case of C_2F_6 and quenching it in the case of C_2F_4. We also point out the appearance of a second maximum in the dependence of the yield on the time delay for rather long values of this variable ($\approx$65 μs). We have related this maximum to the reflection on the cell walls of the energy wave created by the V−T intermolecular relaxation.

Concerning the dissociation and recombination reactions, we have found a competition between the formation of C_2F_6 and the polymer $(CF_2)_n$, induced by changing the frequency of the second IR pulse.

Finally, it has to be remarked that hexafluoropropene has revealed a molecular system whose behavior, in relation to multiphoton dissociation, is modified in a highly noticeable way by rather small changes in the irradiation conditions, suggesting that this molecule is particularly appropiate for the study of the process of multiphoton excitation and dissociation.

Acknowledgment. The authors acknowledge to L. J. Garay, C. L. Sigüenza, P. F. González-Díaz, and L. Díaz for useful discussions. We are largely grateful to the referees for their valuable comments and suggestions. This work has been carried out with financial support provided by the Spanish DGICYT under Project PB93-0145-C02-02.

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