Collisional Relaxation of Highly Vibrationally Excited *cis*-ClFC═CFCl Prepared by Multiphoton Excitation

Eduardo A. Coronado and Juan C. Ferrero*

INFIQC, Departamento de Físicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Agencia Postal 4, C.C. 61, Córdoba 5000, Argentina

Received: August 13, 1997; In Final Form: September 30, 1997⊗

Highly vibrationally excited gas-phase *cis*-ClFC═CFCl was prepared with a pulsed, high-powered pulsed TEA CO_2 laser operating at 948 cm^{-1}, and the subsequent collisional relaxation was followed by infrared fluorescence from the ν_2 mode (1168 cm^{-1}). Energy transfer data were obtained for Ar and ClFC═CFCl molecules as collisional partners. The exponential decay of the average energy together with the linear microcanonical dependence of *I(E)* on $\langle E\rangle$ in a wide energy range allowed for the determination of the dependence of bulk average energy transfer per collision, $\langle\langle\Delta E\rangle\rangle$, on the average energy, $\langle\langle E\rangle\rangle$. In both cases, $\langle\langle\Delta E\rangle\rangle$ is found to be a linear function of $\langle\langle E\rangle\rangle$. As the energy decay profiles are exponential, they are independent of the shape of the initial distribution and of the fraction of molecules excited, allowing one to obtain the dependence of the microscopic first moment of $P(E',E)$, $\langle\Delta E\rangle$, on $\langle E\rangle$. The following dependences of $\langle\Delta E\rangle$ on $\langle E\rangle$ were found:$\langle\Delta E\rangle_P = 4.5 \pm 1.0 - (7.3 \pm 1.5) \times 10^{-3}\langle E\rangle$ cm^{-1} for self-relaxation and $\langle\Delta E\rangle_M = 0.63 \pm 0.06 - (1.0 \pm 0.1) \times 10^{-3} \langle E\rangle$ cm^{-1} for the relaxation with Ar.

Introduction

Collisional energy transfer (CET) of highly vibrationally excited molecules (HVEM) remains one of the most important problems in many chemical as well as photochemical processes. The loss of vibrational energy from HVEM is of particular importance in the field of unimolecular chemical reactions where the collisional deactivation of molecules with chemically significant amount of energy has been studied for roughly seven decades.[1,2]

The interest in this process is due in part to the decisive role it plays in determining the rate at which molecules react to form new products. Early studies were focused in small molecules and low excitation levels with the aim to understand the fundamental process which control the intermolecular energy exchange and the rate and mechanism by which internal modes were equilibrated by collisions.[3−5] These processes are now well understood, in contrast to the relaxation mechanism for HVEM. While the relaxation of molecules at low energy has provided much of the conceptual framework for understanding vibrational energy transfer, it is the high-energy regime that is crucial for a quantitative treatment of unimolecular reactions. The large density of states of HVEM greatly complicates the use of conventional state resolved spectroscopic techniques, although some advances have been recently reported.[6] The collisional relaxation process in the high-energy regime is described in terms of the collisional transition probability $P(E',E)$, for transition from energy E, before collision, to a state with internal energy E', after the collision. The direct measurement of this fundamental function has not yet been performed, although some efforts for its characterization are currently in progress.[7−9]

The choice of molecules amenable to experimental energy transfer studies depends on the availability of adequate techniques to excite them to high vibrational energy levels as well as to monitor the relaxation process. The most commonly used method to prepare HVEM is electronic excitation followed by fast internal conversion to high-lying vibrational levels of the ground electronic state while time-resolved UV absorption (UVA) and infrared fluorescence (IRF) has been applied to follow the energy decay.[10,11] These direct methods yield the bulk average energy transferred per collision, $\langle\langle\Delta E\rangle\rangle$

$$\langle\langle\Delta E\rangle\rangle = \int_0^\infty \langle\Delta E(E)\rangle N(E,t)\, dE \tag{1}$$

where *N(E,t)* is the population distribution function and $\langle\Delta E(E)\rangle$-is:

$$\langle\Delta E(E)\rangle = \int_0^\infty (E' - E)P(E',E)\, dE' \tag{2}$$

The desired quantity is $\langle\Delta E(E)\rangle$, since it is a microscopic property which depends solely on the nature of the collisional partners and not on *N(E,t).* If the initial excitation energy is well-known and the initial energy distribution is narrow enough, it is possible to obtain $\langle\Delta E(E)\rangle$, extrapolating the average energy lost profile at initial time. However as the energy distribution spreads out, only the bulk first moment $\langle\langle\Delta E\rangle\rangle$ can be obtained *directly* from the evolution of the average energy.

In general $\langle\langle\Delta E\rangle\rangle$ is a function of the internal energy, E. In most cases, such as cycloheptatrienes, toluene, azulene, benzene, benzene-d_6, and toluene-d_8, the results of UVA and IRF methods showed that $\langle\langle\Delta E\rangle\rangle$ is almost a linear function of internal energy with a roll-off at the highest energies investigated.[11,12] For some small molecules such as CS_2 and SO_2 the dependence is quadratic over the entire range studied[12,13] while for NO_2 the dependence is *almost* linear up to 4000 cm^{-1} and becomes quadratic and even steeper at higher energies.[14] It should be noted that only for linear dependencies, the relationship between $\langle\langle\Delta E\rangle\rangle$ and $\langle\langle E\rangle\rangle$ is the same than that of $\langle\Delta E\rangle$ on $\langle E\rangle$.

Since the preparation of HVEM in the ground electronic state by UVA is restricted to those molecules with adequate photophysical properties, infrared multiphoton excitation (IRMPE) constitutes a useful alternative method, with the limitation that the initial distribution is poorly characterized and that, in the case of small molecules, could even be bimodal. Notwithstanding, a variety of molecules can be easily excited to different initial energies by simply changing the incident laser fluence.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1997.

Hence, to apply IRMPE to energy transfer studies, it is important to analyze the influence of the distribution function on the determination of $\langle \Delta E \rangle$.

Master equation calculations using unimodal and bimodal initial distributions showed that exponential average energy decays are independent of the shape of *N(E,t)*.[15] In that work, bimodal distributions consisted of a fraction *q* of molecules lying in high vibrational energy levels and the remaining fraction, $1 - q$, populating low vibrational levels. These calculations were performed using the same dependence of $\langle \Delta E \rangle_d$ on $\langle E \rangle$ for both ensembles and showed exponential relaxation, irrespective of the value of *q*. From these theoretical results we concluded that IRMPE could be a useful method to study CET of HVEM, even in the case of bimodal distributions.[15]

In a previous work we have studied the relaxation of $CDCl_3$ prepared by IRMPE and compared different approaches to obtain the microscopic dependence of $\langle \Delta E \rangle$ on $\langle E \rangle$.[16] In that work, the CET process was studied under selected experimental conditions to ensure that bottlenecks to absorption were absent and hence the energy distribution was unimodal.

In this paper we use time-resolved infrared fluorescence to monitor the internal energy content of an intermediate size molecule like *cis*-ClFC=CFCl at energies below the reaction threshold for isomerization. This molecule shows a pressure dependent absorption of IR photons under irradiation with a high-power CO_2 laser indicating the presence of a bimodal initial distribution. The rotational hole is removed at very high pressures, so it is possible to study CET in the presence of variable fractionation. In addition, it presents a strong IR emission from the ν_2 mode at 1168 cm^{-1}, from which the time evolution of the infrared intensity and also the evolution of the average energy could be followed.

Experimental Section

The experimental set up has been described previously.[16] A TEA CO_2 laser tuned to the P(14) line resonant with the ν_9 mode of *cis*-ClFC=CFCl corresponding to 948 cm^{-1} was used as excitation source. The IRF signal was viewed through a NaCl side window by a 1 mm diameter HgCdTe (Infrared Associates) cryogenic photovoltaic detector, sensitive from 5 to 10 μm, equipped with a matched preamplifier.

A 24 cm length, 5 cm diameter Pyrex cell was used. The mode ν_2 at 1168 cm^{-1} was isolated using a MgF_2 window. In all the experiments the IRF signal was amplified using a Tektronik 7633 oscilloscope, digitized with a Thurlby 524 DSA, stored, and averaged with a computer. The laser repetition frequency was 1 Hz.

The laser pulse energy was measured with a Scientech pyroelectric detector and the beam was kept parallel using a set of BaF_2 lenses. A spectrum analyzer (Optical Engineering 16 A) was used to tune the laser to the desired wavelength. All the experiments were performed at a fluence of 1 J cm^{-2}. Pressures were measured with capacitance manometers (ranges 0.001−10 and 0.1−100 Torr). Samples of CFCl=CFCl (Pierce Chem Co.) were degassed and distilled under vacuum before use. FTIR spectrum and gas chromatographic analysis showed that the samples consisted of a mixture of the *cis* and *trans* isomers in a *cis*/*trans* concentration ratio of 0.9. Ar was passed through several traps at 77 K and stored in glass bulbs. The experiments were performed in samples containing 200−700 mTorr of the mixture of isomers with the addition of 2.0−27.0 Torr of Ar as bath gas. To improve the signal/noise ratio, 200−300 IRF curves were averaged. The IRF signals were limited by a 0.5 μs rise time of the infrared detector/preamplifier system and the measured decay rates ranged from 4.8×10^4 to 3.8×10^5 s^{-1}.

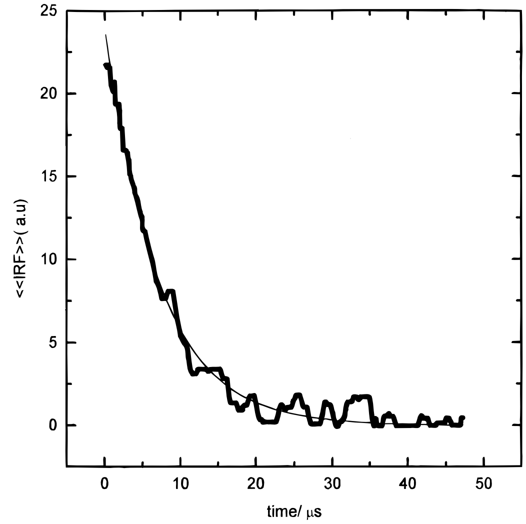

Figure 1. Typical infrared fluorescence decay for the relaxation of *cis*-ClFC=CFCl with Ar at a fluence of 1 J cm^{-2}. ClFC=CFCl and Ar pressures are 0.458 and 14.500 Torr, respectively.

The number of photons absorbed as a function of the Ar pressure was also measured under the same conditions. These measurements were carried out with a dual arrangement of pyroelectric detectors, and the ratio of the transmitted to the incident intensity was obtained by a Scientech power ratio meter, averaging at least 20 signals in every case.

Results and Discussion

Previous studies performed with a mixture of *cis*- and *trans*-ClFC=CFCl showed that the *cis* isomer could be selectively excited to yield *trans*-ClFC=CFCl with a low reaction probability (10^{-2}), even at relatively high energy fluences (5 J cm^{-2}).[17] Since the present experiments were performed at a lower fluence (1 J cm^{-2}) and with a mixture of both isomers diluted in Ar, the IRF lost profile could be considered free of any chemical process.

A typical IRF decay is shown in Figure 1. The signals followed single-exponential functions of the type:

$$\langle\langle I(E,t)\rangle\rangle = A + B \exp(-rt) \tag{3}$$

where $\langle\langle I(E,t)\rangle\rangle$ is the macroscopic IRF intensity, which is an average of the microcanonical intensity *I(E)* of the observed vibrational mode over the excited energy distribution *N(E,t)*, and *r* is the relaxation rate. The microcanonical IRF intensity, *I(E)*, is related to the internal energy content of the molecule by the following equation, due to Durana and McDonald.[18]

$$I(E) = \frac{1}{\rho_s(E)} h\nu_i A^{1,0} \sum_{n=1}^{\text{modes}} n_i \rho_s(E - n_i h\nu_i) \tag{4}$$

where $A^{1,0}$ is the Einstein coefficient for spontaneous emission for the 1−0 transition of the *i*th mode, $h\nu_i$ is the energy of the emitted photon, and ρ_s(E) and $\rho(E - n_i h\nu_i)$ are the density of vibrational states for all *s* oscillators at energy *E* and that for $s - 1$ modes, respectively, omitting the emitting mode and energy contained in it. For the υ_2 mode of cis- ClFC=CFCl the relationship between *I(E)* and $\langle E \rangle$, calculated according to eq 4, was found to be linear over a wide energy range (2000−40000 cm^{-1}). As a consequence, the observed intensity $\langle\langle I(E,t)\rangle\rangle$, is also a linear function of the average energy $\langle\langle E \rangle\rangle$, that is

$$\langle\langle I(E,t)\rangle\rangle = I(\langle\langle E\rangle\rangle,t) = r + s\langle\langle E\rangle\rangle \tag{5}$$

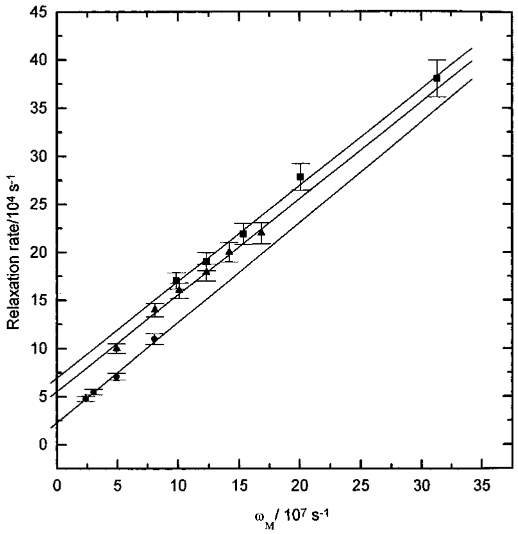

Figure 2. Relaxation rates for different pressures of the mixture of *cis*- and *trans*-ClFC=CFCl as a function of Ar collisional frequency at a fluence of 1 J cm^{-2}. (■) 0.700 Torr, (△) 0.458 Torr of ClFC=CFCl, (○) 0.240 Torr.

Combining eqs 3 and 5 results in

$$\langle\langle E\rangle\rangle = C + D\exp(-rt) \tag{6}$$

where $C = A - r/s$ and $D = B/s$. Then the average energy decay is also exponential with the same relaxation rate r as the IRF decay. From this decay the energy dependence of the bulk average energy transferred can be obtained from the exact expression[19]

$$-\frac{\mathrm{d}\langle\langle E\rangle\rangle}{\mathrm{d}t} = \omega\langle\langle \Delta E\rangle\rangle \tag{7}$$

where ω is the collisional frequency.

As the energy lost profiles are exponential, the dependence of $\langle\langle \Delta E\rangle\rangle$ on $\langle\langle E\rangle\rangle$ is linear:

$$\langle\langle \Delta E\rangle\rangle = a + b\langle\langle E\rangle\rangle \tag{8}$$

Then, combining eqs 7 and 8, the evolution of the average energy is given by

$$\langle\langle E\rangle\rangle = -\frac{a}{b} + \left(\langle\langle E\rangle\rangle_0 + \frac{a}{b}\right)\exp(-b\omega t) \tag{9}$$

where $\langle\langle E\rangle\rangle_0$ is the initial average energy of the excited molecules.

Comparing eq 6 with eq 9 we identify the relaxation rate as $r = b\omega$. Thus the coefficient b is obtained directly from the IRF decay rate.

When the system reaches the equilibrium Boltzmann energy distribution, $\langle\langle \Delta E\rangle\rangle = 0$. This corresponds to the limit $t \rightarrow \infty$ in eq 9, which yields

$$\langle\langle E\rangle\rangle_\infty = -\frac{a}{b} \tag{10}$$

Since the coefficient b can be obtained from the relaxation rate r, the coefficient a is calculated from eq 9 provided that $\langle\langle E\rangle\rangle$, the average energy of the Boltzmann distribution at the temperature of the experiment, is known.

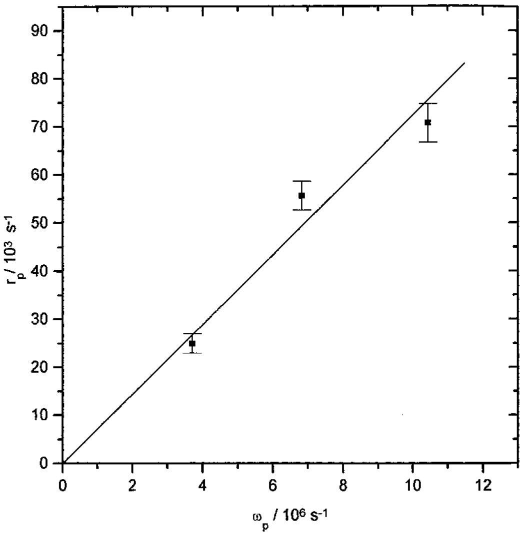

Figure 3. Relaxation rates obtained from the zero intercept of Figure 3 as a function of ClFC=CFCl collisional frequency.

TABLE 1: Lennard-Jones Parameters for the Collisional Partners

species	σ/Å	ϵ/K
ClFC=CFCl	5.50	364
Ar	3.47	114

TABLE 2: Relaxation Rates r_P and Coefficient b_M Obtained from Figure 3 for Each Pressure of ClFC=CFCl

pressure of the mixture of *cis/trans*-ClFC=CFCl (mTorr)	$r_P/10^3$ (s^{-1})	$b_M/10^{-5}$	$a_M/10^{-2}$ (cm^{-1})	$b_P/10^{-4}$	$a_P/10^{-1}$ (cm^{-1})
240	25 ± 2	100 ± 2	63 ± 1	70 ± 6	44 ± 4
460	56 ± 3	102 ± 5	64 ± 3	81 ± 5	50 ± 3
700	70 ± 4	100 ± 3	63 ± 2	67 ± 4	42 ± 3

The relaxation rates for different pressures of ClFC=CFCl as a function of collisional frequency of added Ar are shown in Figure 2. The global relaxation rate r is expected to be the sum of two contributions ("linear mixing rule"): the self-relaxation of ClFC=CFCl by collisions with cold *cis* and *trans* molecules, r_P, and the relaxation with Ar, r_M.

$$r = r_M + r_P = \omega_M b_M + \omega_P b_P \tag{11}$$

ω_M and ω_p are the collisional frequencies for Ar and ClFC=CFCl, respectively. The collisional numbers used to convert pressure to collisional frequencies were 1.16×10^7 and 1.5×10^7 Torr^{-1} s^{-1} for collisions of ClFC=CFCl with Ar and with ClFC=CFCl, respectively. The Lennard-Jones parameters are shown in Table 1. Figure 2 shows that the global relaxation rate is a linear function of Ar collisional frequency, for each ClFC=CFCl pressure, in agreement with eq 11. Equation 11 also predicts that all the straight lines of Figure 2 must have the same slope (b_M) for each substrate pressure. A least-squares fit to the experimental points yielded the values of b_M and r_P at each pressure of ClFC=CFCl. A plot of r_P as a function of collisional frequency of ClFC=CFCl also yielded a straight line with approximately zero intercept, from whose slope the value of b_p was obtained (Figure 3).

The values of r_P, b_P, a_P, b_M, and a_M are shown in Table 2. Assuming that the linear mixing rule is valid, then

$$\langle\langle \Delta E\rangle\rangle = \frac{\omega_P}{\omega_M + \omega_P}\langle\langle \Delta E\rangle\rangle_P + \frac{\omega_M}{\omega_M + \omega_P}\langle\langle \Delta E\rangle\rangle_M \tag{12}$$

As the decays are exponential for all the mixtures ratios of parent and bath gas, $\langle\langle \Delta E\rangle\rangle$ for both species should be linearly dependent on $\langle\langle E\rangle\rangle$,

$$\langle\langle \Delta E\rangle\rangle_M = a_M + b_M\langle\langle E\rangle\rangle \tag{13}$$

$$\langle\langle \Delta E\rangle\rangle_P = a_P + b_P\langle\langle E\rangle\rangle \qquad (14)$$

where a_P and a_M are the values that make $\langle\langle \Delta E\rangle\rangle = 0$ at thermal equilibrium.

When the system reaches equilibrium, $\langle\langle E\rangle\rangle = \langle\langle E\rangle\rangle_\infty$ and $\langle\langle \Delta E\rangle\rangle = 0$. With this condition and replacing eqs 13 and 14 in eq 12 results in

$$\langle\langle \Delta E\rangle\rangle = \frac{\omega_P}{\omega_M + \omega_P}(a_M + b_M\,\langle\langle E\rangle\rangle_\infty) + \frac{\omega_M}{\omega_M + \omega_P}(a_P + b_P\,\langle\langle E\rangle\rangle_\infty) = 0 \qquad (15)$$

so that

$$\langle\langle E\rangle\rangle_\infty = -\left(\frac{a_M\omega_M + a_P\omega_P}{b_M\omega_M + b_P\omega_P}\right) = -\frac{a_M}{b_M} = -\frac{a_P}{b_P} \qquad (16)$$

The value of $\langle\langle E\rangle\rangle$ for *cis*-ClFC=CFCl calculated from a Boltzmann equilibrium at 298 K is 629 cm^{-1}, which together with the values of b_M and b_P allowed for the calculation of the coefficients a_M and b_M from eq 16, so that the following expression for the dependence of $\langle\langle \Delta E\rangle\rangle$ on $\langle\langle E\rangle\rangle$ are obtained, for each collisional partner:

$$\langle\langle \Delta E\rangle\rangle_P = 4.5 \pm 1.0 - (7.3 \pm 1.5) \times 10^{-3}\langle\langle E\rangle\rangle\ \mathrm{cm}^{-1} \qquad (17)$$

$$\langle\langle \Delta E\rangle\rangle_M = 0.63 \pm 0.06 - (1.0 \pm 0.1) \times 10^{-3}\langle\langle E\rangle\rangle\ \mathrm{cm}^{-1} \qquad (18)$$

Note that the data obtained for self- relaxation results from collisions of excited *cis*-ClFC=CFCl with both *cis* and *trans* isomers.

In the above analysis, a macroscopic property, i.e., the dependence of $\langle\langle \Delta E\rangle\rangle$ on $\langle\langle E\rangle\rangle$, was obtained from a knowledge of the bulk relaxation rate at different collisional frequencies of the bath gas. Now two important points arise concerning the energy range where this dependence holds and whether the macroscopic dependence of $\langle\langle \Delta E\rangle\rangle$ on $\langle\langle E\rangle\rangle$ is equal to the microscopic dependence of $\langle \Delta E\rangle$ on $\langle E\rangle$.

An answer to the first point requires a knowledge of the average energy of the initial distribution. To accomplish this, the average number of photons absorbed per molecule were measured under the same experimental conditions as the IRF relaxation experiments. The results are shown in Figure 4. The average number of photons absorbed per molecule increases with pressure as a consequence of rotational hole filling, allowing that a larger fraction of molecules interacts with the laser. At high enough pressures, when rotational relaxation is fast compared with the rate of laser pumping, a unimodal energy distribution is formed, but at pressures below this limit only a fraction of molecules interacts with the laser. Then $\langle n\rangle$ represents a mean value over the whole ensemble, but it does not necessarily provides a direct measurement of the average energy of the fraction of absorbing molecules.

In general, if q is the fraction of molecules excited with average energy $\langle\langle E\rangle\rangle_q$, the average energy of the whole ensemble would be

$$\langle\langle E\rangle\rangle = q\langle\langle E\rangle\rangle_q + (1 - q)\langle\langle E\rangle\rangle_{1-q} \qquad (19)$$

where $\langle\langle E\rangle\rangle_{1-q}$ is the average energy of the fraction $(1 - q)$ of molecules that remain in low vibrational energy states.

An additional complication in the determination of the initial average energy could be introduced by V−T processes, during the pulse. Considering that the laser pulse length is about 200 ns, at a collisional frequency of 1 × 10^8 s^{-1} the parent molecules suffer about 20 gas kinetics collisions during the process of excitation. Modeling calculations performed for molecules of similar type showed that the absorption process occurs in the first 200 ns and that it is not affected by energy transfer to Ar during the laser pulse.[16] In the present case, from the experimental relaxation rates it can be deduced that at $t = 200$ ns, the energy has fallen, at most, to 0.93 its initial value, even in the most favorable experimental conditions for vibrational relaxation used (0.7 Torr of ClFC=CFCl and 27 Torr of Ar). Thus we conclude that the measured value of $\langle n\rangle$ is not seriously affected by the relaxation process. The absorption measurement shows that $\langle n\rangle$ varies between 7 and 15, which corresponds to average excitation energies in the range 7000−15000 cm^{-1}. Note, however, that if only a fraction of molecules is excited, then $\langle n\rangle$ is distributed only on this fraction and consequently the excitation energy $\langle\langle E\rangle\rangle_q$ should be higher. Thus the above-mentioned energy range represents a lower limit to the true initial value.

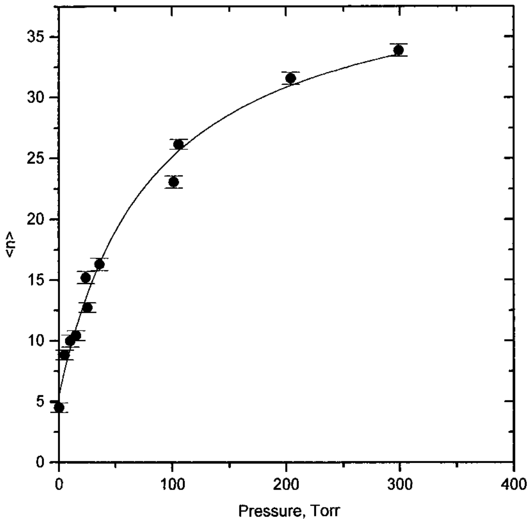

Figure 4. Average number of photons absorbed per molecule as a function of Ar pressure at a fluence of 1 J cm^{-2} and a pressure of 0.220 Torr of the mixture of *cis*- and *trans*-ClFC=CFCl.

The second point has been the subject of some discussion.[15,19] For exponential average energy decays, the microscopic dependence of $\langle \Delta E\rangle$ on $\langle E\rangle$ is independent of the shape of the initial distribution. Model calculations showed that if $\langle \Delta E\rangle$ is linearly dependent on $\langle E\rangle$ the energy decay is exponential and independent of the fraction q of molecules excited.[15] As the decays are exponential at all the pressures investigated, it follows that the dependence of $\langle \Delta E\rangle$ on $\langle E\rangle$ can be extracted even in the case that the fraction q and consequently $\langle\langle E\rangle\rangle_q$ varies. This fact can be rationalized taking the time derivative of eq 19

$$\frac{d\langle\langle E\rangle\rangle}{dt} = q\frac{d\langle\langle E\rangle\rangle_q}{dt} + (1 - q)\frac{d\langle\langle E\rangle\rangle_{1-q}}{dt} \qquad (20)$$

$$= q\langle\langle \Delta E\rangle\rangle_q + (1 - q)\langle\langle \Delta E\rangle\rangle_{1-q} \qquad (21)$$

where $\langle\langle \Delta E\rangle\rangle_q$ and $\langle\langle \Delta E\rangle\rangle_{1-q}$ represent the average energy transferred by the ensemble of molecules having average energy $\langle\langle E\rangle\rangle_q$ and $\langle\langle E\rangle\rangle_{1-q}$, respectively. As the average energy decay of the whole ensemble is exponential, the coefficients of the energy dependence of $\langle\langle \Delta E\rangle\rangle_q$ and $\langle\langle \Delta E\rangle\rangle_{1-q}$ must be linear functions of $\langle\langle E\rangle\rangle$, i.e.

$$\langle\langle \Delta E\rangle\rangle_q = a_1 + b_1\langle\langle E\rangle\rangle \qquad (22)$$

$$\langle\langle \Delta E\rangle\rangle_{1-q} = a_2 + b_2\langle\langle E\rangle\rangle \qquad (23)$$

TABLE 3: Collisional Efficiencies for Relaxation with Ar

substrate	$\gamma/10^{-3}$	$g(E)_{\mathrm{quant}}$	g_{class}	$\gamma_{\mathrm{int(quant)}}/10^{-3}$	$\gamma_{\mathrm{int(class)}}/10^{-3}$	ν_{min} (cm^{-1})	ref
cis-ClFC═CFCl	1.1 ± 0.2	0.11^{a}	0.083	10 ± 2	13.7 ± 2.4	150	this work
CF_2Cl_2	1.2 ± 0.1^{f}	0.13^{b}	0.11	9.2 ± 0.8	10.8 ± 0.9	260	27
	1.0 ± 0.3^{g}			9 ± 3	9.0 ± 2.7		26
	0.5^{h}			3.8	4.5		28
	1.70 ± 0.03^{i}			13.0 ± 0.2	15.3 ± 0.3		25
1,2 -$C_2F_4Cl_2$	14 ± 1^{f}	0.077^{c}	0.055	182 ± 13	252 ± 18	< 90	27
1,2- $C_3F_6Cl_2$	20 ± 2^{f}	0.064^{d}	0.037	312 ± 31	540 ± 54	< 90	27
C_3F_8	7.6 ± 0.1^{i}	0.064^{e}	0.037	119 ± 1.6	205 ± 2.7	86	25

[a] The normal mode frequencies were taken from ref 32. [b] The normal mode frequencies were taken from ref 33. [c] The calculation is approximate, since the normal mode frequencies used are those corresponding to 1,1-$C_2F_4Cl_2$ (ref 34). [d] The normal mode frequencies were supposed to be the same as those of C_3F_8. [e] The normal mode frequencies were taken from ref 35. [f] Obtained by Setser et al. looking at populations depletions produced by reactions of vibrationally excited CF_2Cl_2.[27] [g] Thermal lensing experiments by Xu et al.[26] [h] IR emission experiments of Karve et al.[27] [i] Time-resolved optoacustic experiments of Tardy et al.[25,27]

Thus, the experimentally determined coefficient *b*, which is independent of pressure, is a linear combination of the microscopic coefficients b_1 and b_2, weighted by the fraction of molecules in each ensemble, i.e.

$$b = qb_1 + (1 - q)b_2 \tag{24}$$

Since *q* changes with pressure while *b* remains constant, it follows that:

$$qb_1 + (1 - q)b_2 = q'b_1 + (1 - q')b_2 \tag{25}$$

where *q* and *q*′ represent different fractions of absorbing molecules. Equation 25 holds only if $b_1 = b_2$, which implies, from eq 24, that they are also equal to *b*. That is both ensembles relaxes with the same coefficient. This situation corresponds to the observations of the present experiments, since although the fraction of molecules changes with pressure, the coefficient *b* remains the same.

Note that at different pressures of ClFC═CFCl, parallel straight lines are obtained, which implies that the linear sum rule (eq 11) is valid in all the pressure range investigated.

A more significant magnitude than $\langle \Delta E \rangle$ is the average of deactivating collisions $\langle \Delta E \rangle_d$.[19] However, it cannot be directly obtained from experiment but could be calculated from $\langle \Delta E \rangle$ provided that the collisional transition probabilities were known. Since this is not feasible, calculations of $\langle \Delta E \rangle_d$ rely on a reasonable choice of $P(E',E)$. A frequently used function is the simple exponential transition probability model, defined as

$$P(E',E) = N(E) \exp\left(\frac{E' - E}{\alpha}\right) \qquad \text{for } E' < E \tag{26}$$

where α is almost equal to $\langle \Delta E \rangle_d$. Using this model together with eqs 17 and 18, the dependence of $\langle \Delta E \rangle_d$ on *E* results[21−22]

$$\langle \Delta E \rangle_d = 76 + 9.3 \times 10^{-3} \langle E \rangle \text{ cm}^{-1} \tag{27}$$

for the self-relaxation and

$$\langle \Delta E \rangle_d = 33 + 2.2 \times 10^{-3} \langle E \rangle \text{ cm}^{-1} \tag{28}$$

for relaxation with Ar.

No attempt was made to use other currently used functions for $P(E',E)$, such as biexponential models,[23] since it has been shown that for linear dependencies there is always a set of different $P(E',E)$ functional shapes that yields the same dependence of $\langle \Delta E \rangle_d$ on $\langle E \rangle$.[24]

To compare energy transfer data with related compounds, it is useful to compare them in terms of collision efficiencies, which is defined as[25]

$$\gamma = -\frac{\langle \Delta E \rangle}{\langle E \rangle} \tag{29}$$

For a linear energy dependence it also results that

$$\gamma = -\frac{\langle\langle \Delta E \rangle\rangle}{\langle\langle E \rangle\rangle} \tag{30}$$

The coefficients b_P and b_M of the linear dependence are calculated from the experimental relaxation rates (r_P and r_M) provided the collisional frequencies ω_P and ω_M are known. The choice of ω is empirical but since they affect directly the collisional efficiencies, caution must be taken when comparisons are made. For halogenated substrates it is a common practice to use hard-sphere collisional frequencies. As we have used Lennard-Jones collisional frequencies, the above values of the coefficients of the linear dependence of $\langle\langle \Delta E \rangle\rangle$ must be corrected by a factor of 1.56 and 1.25 for the self-relaxation and for the relaxation with Ar, since the hard sphere collisional numbers used to convert pressures to collisional frequencies are 0.96×10^7 and 0.93×10^7 Torr s^{-1}, respectively. With this correction, at 8000 cm $^{-1}$ $\gamma = (1.0 \pm 0.2) \times 10^{-2}$ for the self-relaxation and $\gamma = (1.1 \pm 0.2)\ 10^{-3}$ for Ar as colliding pair.

To our knowledge, there is not energy transfer data for *cis*-ClFC═CFCl, so that a direct comparison of our results with that obtained by other techniques is not possible. Table 3 presents the values of γ together with that reported, using different techniques, for other halogenated substrates, for the relaxation with Ar.

Although a comparison is not straightforward, a simple model presented by Tardy[25] *et al.* about the influence of the complexity of the substrate on the value of γ could be helpful. According to this model, the relaxation of a polyatomic molecule is considered as contributions from all oscillators with their energies "frozen" before collision so that the rate constant for V−T relaxation is:

$$k_{V-T} = \sum_i \sum k_{V-T}(i,E_i)\, f(i,E_i) \tag{31}$$

where the sum is extended over all the vibrational modes such that $\sum_i E_i = E$ and $f(i,E_i)$ is the fraction of the *i*th mode oscillator which contains energy E_i. The double sum may be reduced to a single sum if $k_{V-T}\, f(i,E_i)$ for one mode is larger than all the others; there is a doorway oscillator. $f(i,E_i)$ depends upon the complexity of the vibrational frequencies of the substrate. Depending upon specific limiting conditions, the number of terms in the double sum of eq 31 may be reduced to a sum up to a threshold, at which point the high-frequency modes due to both small values of k_{V-T} and low E_i do not contribute to the relaxation. A large polyatomic molecule is considered as having one active oscillator (presumably the one with the lowest vibrational frequency, since this would give a more impulsive and more efficient collision) embedded in an energy source comprised of the remaining oscillators. The deactivation of a polyatomic with an average energy $\langle E\rangle$ by a collision with an atom is reduced to the relaxation of a pseudo-diatomic molecule with an energy $\langle E\rangle_{\rm osc}$. This simple model is supported by the results of trajectory calculations for the relaxation of vibrationally excited azulene, which indicate that only the lowest vibrational frequencies are involved in the relaxation process.[29]

Assuming a rapid exchange of energy between oscillators, the energy in the low-frequency mode before collision can be written as $\langle E\rangle_{\rm osc} = g(E)\,\langle E\rangle$, using quantum statistics to calculate the factor $g(E)$. The relaxation oscillator has an intrinsic efficiency $\gamma_{\rm int}$ that is a function of $\langle E\rangle_{\rm osc}$; i.e.

$$\gamma_{\rm int} = -\frac{\langle \Delta E\rangle}{\langle E\rangle_{\rm osc}} \qquad (32)$$

As $\langle \Delta E\rangle$ is a linear function of $\langle E\rangle$, it follows from eqs 10 and 31 that

$$\gamma_{\rm int} = -\frac{a + b\langle E\rangle}{\langle E\rangle_{\rm osc}} = -\frac{b}{g(E)}\left(1 - \frac{\langle E\rangle_{\infty}}{\langle E\rangle}\right) \cong -\frac{b}{g(E)} \qquad (33)$$

Thus, $\gamma_{\rm int}$ is almost independent of the energy located on the relaxation oscillator and will be an intrinsic property of that oscillator depending mainly on its frequency. According to SSH theory, $\gamma_{\rm int}$ must be an inverse function of its frequency.

The observed efficiency, $\gamma_{\rm obs}$, is related to $\gamma_{\rm int}$ by

$$\gamma_{\rm obs} = -g(E)\frac{\langle \Delta E\rangle}{\langle E\rangle_{\rm osc}} = g(E)\gamma_{\rm int} \qquad (34)$$

In this way $\gamma_{\rm int}$ is obtained dividing $\gamma_{\rm obs}$ by the fraction of energy that resides in the relaxation oscillator. Classical equipartition of energy predicts that energy will be partitioned equally between all modes. As Toselli and Barker have pointed out the breakdown of classical equipartition of energy can skew the apparent results of classical trajectory calculations.[30] For this reason, we have calculated $g(E)$ for the lowest frequency mode at $\langle E\rangle = 8000$ cm^{-1} using quantum statistics, $g(E)_{\rm quant}$, and also using the classical approximation, $g_{\rm class} = 1/n_{\rm osc}$, being $n_{\rm osc}$ the number of normal modes of the molecule.

The intrinsic efficiencies for relaxation with Ar, calculated according to eq 33 are shown in Table 3. Note that, for the same molecule, the quantum intrinsic efficiency $\gamma_{\rm int(quant)}$ shown in Table 3 is smaller than the classical intrinsic efficiency, $\gamma_{\rm int(class)}$. This is due to the fact that the lowest frequency mode always receive less energy than predicted by classical statistics.

It is observed, as expected, that the fraction of energy which resides in the relaxation oscillator decreases with the complexity of the substrate. This effect may produce a decrease $\gamma_{\rm obs}$, opposed to the experimental observations. However the frequency of the lowest frequency modes of these molecules is the main factor controlling the intrinsic efficiency. With this assumption, it seems reasonable that the intrinsic efficiency of *cis*-ClFC═CFCl is lower than that of the halogenated ethanes and propane, since these molecules have lower frequencies.

When comparing molecules with almost the same frequency patterns the main factor controlling the relaxation is $g(E)$. This fact was nicely shown by Tardy[31] et al. in the series going from C_3F_8 to C_8F_8. In this context, $\gamma_{\rm int}$ should be almost the same for all the halogenated ethanes and propanes given in Table 3, provided they have almost the same lowest frequency. The discrepancies observed in the intrinsic efficiencies for these molecules are not easy to explain. Note, however, that the classical values of $\gamma_{\rm int(class)}$ for 1,2-$C_2F_4Cl_2$ and C_3F_8 are in better agreement than the quantum values.

The comparison with CF_2Cl_2 is not very clear, since the values do not differ too much, (even using quantum statics to calculate the factor $g(E)$) despite the lower frequency of the relaxation oscillator of *cis*-ClFC═CFCl. The differences may be due to experimental errors or that there is not only one factor determining the relaxation efficiency.

The interpretation of when the deactivator is polyatomic, becomes more complex since it contains other energy sinks as vibration and rotation. The values of $\gamma_{\rm int(quant)}$ and $\gamma_{\rm int(class)}$ for the self-deactivation of *cis*-ClFC═CFCl are 9×10^{-2} and 12×10^{-2} respectively. These values are almost equal to that obtained for the self-relaxation of CF_2Cl_2 measured by time-resolved optoacustic[25] ($\gamma_{\rm int(quant)} = 11.5 \times 10^{-2}$ and $\gamma_{\rm int(class)} = 13.6 \times 10^{-2}$) and thermal lensing[26] ($\gamma_{\rm int(quant)} = 12 \times 10^{-2}$ and $\gamma_{\rm int(class)} = 10 \times 10^{-2}$). Note, however, that $\gamma_{\rm int}$ for the self-relaxation is greater by a factor of 10 compared with $\gamma_{\rm int}$ for the deactivation with Ar.

Conclusions

This study shows that when the relaxation rates are obtaining in conditions where a bimodal energy distribution is formed the dependence of $\langle \Delta E\rangle$ on E can be obtained for exponential decays of $\langle\langle E\rangle\rangle$, under certain conditions. In this respect, we have shown that if the experimental coefficient b of the linear dependence of $\langle \Delta E\rangle$ on $\langle E\rangle$ is independent of the fraction of excited molecules, both components of the distribution must have the same dependence of $\langle \Delta E\rangle$ on $\langle E\rangle$. This was experimentally observed for the collisional relaxation of *cis*-ClFC═CFCl with Ar as bath gas and allowed for the determination of the microscopic dependence of $\langle \Delta E\rangle$ on $\langle E\rangle$.

The linear sum rule (eq 11) was verified experimentally, and microscopic CET data was also obtained for the self -relaxation of the parent molecule. The values of $\gamma_{\rm int}$ for the relaxation with Ar can be compared with related substrates considering that there is a doorway oscillator, the one with the lowest frequency, controlling the overall rate of relaxation.

Acknowledgment. The authors thank CONICET and CONICOR for financial assistance and the European Union (Contract CI1*-CT94-0128, DG12HSMV).

References and Notes

(1) Tardy, D. C.; Rabinovitch, B. S. *Chem. Rev. (Washington, D.C.)* **1977**, *77*, 369.

(2) Oref, I.; Tardy D. C. *Chem. Rev.* **1990**, *90*, 1407.

(3) Sheorey, R. S.; Flynn G. W. *J. Chem. Phys.* **1973**, *58*, 1467. Weitz, E.; Flynn, G. W. *Annu. Rev. Phys. Chem.* **1964,** *41*, 1883.

(4) Stephenson, J. C.; Moore, C. B. *J. Chem. Phys.* **1972**, *56*, 1295.

(5) Stephenson, J. C.; Finzi, J.; Moore, C. B. *J. Chem. Phys.* **1972**, *56*, 5214.

(6) Hartland, G. V.; Qin, D.; Dai, H. L. *J. Chem. Phys.* **1995**, *102*, 8677.

(7) Lenvay, G.; Schatz, G. C. *J. Phys. Chem.* **1994**, *98*, 6530.

(8) Mullin, A. S.; Michaels, C. A.; Flynn, G. W. *J. Chem Phys.* **1995**, *102*, 6032.

(9) Luther, K.; Reihs, K. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 442.

(10) Hippler, H.; Troe, J. In *Bimolecular Collisions*; Ashfold, M. N. R., Ed.; The Royal Society of Chemistry: London, 1989; p 209.

(11) Toselli, B. M.; Barker, J. R. *Int. Rev. Phys. Chem.* **1993** *12*, 305.

(12) Dove, J. E.; Hippler H.; Troe J. *J. Chem. Phys.* **1985**, *82*, 1907.

(13) Heymann, M.; Hippler H.; Plach J. J.; Troe J. *J. Chem. Phys.* **1987**, *87*, 3867. Heymann, M.; Hippler H.; Nahr, D.; Troe J. *J. Phys. Chem.* **1988**, *92*, 5507.

(14) Toselli, B. M.; Walunas, T. L.; Barker J. R. *J. Chem. Phys.* **1990**, *92*, 4793.

(15) Coronado, E. A.; Rinaldi, C. A.; Velardez, G. F.; Ferrero, J. C. *Chem. Phys. Lett.* **1994,** *227*, 164.

(16) Rinaldi, C. A.; Ferrero, J. C.; Vázquez, M. A.; Azcárate, M. L.; Quel, E. J. *J. Phys. Chem.* **1996**, *100*, 9745.

(17) Coronado, E. A.; Ferrero, J. C. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1991**, *103*, 455.

(18) Durana, J. F.; Mc Donald, J. D. *J. Chem. Phys.* **1976**, *64*, 2518.

(19) Forst, W. *Advances in Chemical Kinetics and Dynamics;* Barker, J. R., Ed.; London, England, 1995; Vol. 2B.

(20) Gilbert, R. G.; Smith S. C. *Theory of Unimolecular and Recombination Reactions;* Blackwell: Oxford, 1990.

(21) Barker, J. R.; Golden, R. E. *J. Phys. Chem.* **1984,** *88*, 1012.

(22) Whitten, G. Z.; Rabinovitch, B. S. *J. Chem. Phys.* **1964,** *41*, 188.

(23) Troe, J. *J. Chem. Phys*. **1992**, *97*, 288.

(24) Coronado, E. A.; Ferrero J. C. *Chem. Phys. Lett.* **1996**, *257*, 674.

(25) Tardy, D. C. *J. Phys. Chem.* **1993**, *97*, 5624.

(26) Ma, Y.; Xu, Z. *Chem. Phys. Lett.* **1983**, *98*, 563.

(27) Sobczinski, R.; Setser D. W.; Slage A. R. *J. Chem. Phys.* **1990**, *92*, 1132.

(28) Karve, R. S.; Sarker, S. K.; Rama Rao, K.V. S.; Mittal, J. V. *Spectrochim. Acta* **1987**, *43A*, 165.

(29) Clarke, D. L.; Gilbert, R. G. *J. Phys. Chem.* **1992**, *96*, 8450.

(30) Toselli, B. M.; Barker, J. R. *Chem. Phys. Lett*. **1990**, *174*, 304.

(31) Tardy, D. C.; Song B. H. *J. Phys. Chem.* **1993**, *97*, 5628.

(32) Craig, N. C.; Evans, D. A. *J. Am. Chem. Soc.* **1965**, *87*, 4223.

(33) Claassen, H. H. *J. Chem. Phys.* **1954**, *22*, 50.

(34) Nielsen, J. R.; Liang, C. Y.; Smith, R. M.; Smith D. C. *J. Chem. Phys.* **1953**, *21*, 383.

(35) Bürger, H.; Pawelke, G. *Spectrochim. Acta* **1979**, *35A*, 525.