

MODELING THE VIBRATIONAL RELAXATION OF POLYATOMIC MOLECULES. THE METHYLFLUORIDE CASE STUDY

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We present in this paper a theoretical analysis of the vibrational translational (V–T) relaxation process in CH₃F, carried out by using a numerical model based on rate equations. In particular, we have analysed the dependence of the V–T relaxation time on the average vibrational energy absorbed per molecule. We have also investigated the influence of the dependence of the rate constants used in the model, on the gas translational temperature. The results of the model clearly outline the strongly nonlinear character of the V–T relaxation process in CH₃F, a situation commonly observed in other important polyatomic molecules of intermediate size each as SF₆, freons, and related methylhalides.

KEY WORDS: Multiphoton excitation; non linear relaxation.

1. INTRODUCTION

In the last period, a number of papers has dealt with the gas phase collisional energy transfer in the electronic ground state of highly excited polyatomic molecules. The interest lies both in large polyatomics such as azulene, toluene, benzene, and smaller ones such as SF₆, fluorochloromethanes, SiF₄ (see¹ for a review). In most of these experiments the key quantity measured is the average vibrational energy transferred per collision, $\langle \Delta E \rangle$ and its dependence on the average vibrational energy $\langle E \rangle$ initially stored by some means in one molecule. Often the results are a source of controversy and the dynamical factors governing this dependence are still under investigation, both experimentally and theoretically.

While in the low excitation regime the semiclassical Schwartz-Slawsky-Herzfeld (SSH) theory² provides good explanations of the data, a great effort is currently made in order to model and to understand the vibrational–vibrational (V–V) inter and intramolecular relaxation as well as the vibrational–translational (V–T) dynamics for excitation energies ranging from close to the dissociation threshold down to the nearly thermal energies.^{3–6} For example recent Monte-Carlo computer simulations for highly excited CS₂ in Ar³ were able to predict for $\langle \Delta E \rangle$ values which are close to the experimental ones.⁶ The model yielded a linear dependence of $\langle \Delta E \rangle$ on $\langle E \rangle$ for the whole investigated energy range. However, for CS₂, as for many polyatomic molecules, the $\langle \Delta E \rangle$ dependence on $\langle E \rangle$ shows a linear dependence

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in the low $\langle E \rangle$ range (up to 6000 cm^{-1}), followed by a stronger than linear dependence (where the V-T relaxation time is observed to decrease), and, finally, again a linear dependence in the high energy region (above $16,000 \text{ cm}^{-1}$). The same behaviour has been evidenced for SF_6 ⁴ and CF_2HCl ⁵, although the above mentioned energy thresholds were found around 1000 and 4000 cm^{-1} , respectively.

The CH_3F molecule has been studied intensively for its interesting properties concerning the V-V relaxation, but also for its prospective use in the passive mode locking of the CO_2 laser,⁷ FIR radiation generation⁸ and its possible applications concerning chemical and isotopic selectivity.⁹

The ν_3 C-F stretching mode has the fundamental (1081 cm^{-1}) resonant to the P(20) CO_2 laser line, and, in the same time, is the lowest vibrational frequency which is believed to be the "doorway" for the V-T relaxation.¹ The slow V-T relaxation caused by the high ν_3 value makes it possible to store the vibrational energy in the various vibrational modes for a relatively long period. The laser induced fluorescence (LIF) techniques make thus it possible to study in great detail the intra- and inter-mode V-V relaxation and to measure the appropriate rate constants (see¹⁰⁻¹² and references cited therein). The V-T relaxation rate was also measured by LIF, double resonance, and thermal lens techniques. High resolution spectroscopy¹³ revealed the existence of Fermi resonances and Coriolis interaction between the high vibrational levels $3\nu_3 \leftrightarrow \nu_4$ and $(2\nu_2, 2\nu_5) \leftrightarrow 3\nu_3$. As a result the main rate constants for the vibrational energy exchange and transformation are rather well established.

The most natural way for a theoretical investigation of the relaxation phenomena in CH_3F was thus to use these rate constants in kinetic models based on a given structure of the vibrational levels and on coupled rate equations for their population evolution. Indeed, such kinetic models^{11,12} were able to reproduce the LIF results and also to predict¹² V-V rates for higher vibrational levels.

In the present paper we shall present the results obtained by adapting the model of Nakane and Tsuchiya,¹² hereafter called NT model, to the study of vibrational-translational relaxation processes. The NT model was originally developed for studying V-V intra- and inter-molecular relaxation in CH_3F . In particular, we have paid great attention to the V-T relaxation time (TVT) dependence on $\langle E \rangle$, and we have also analyzed the dependence of $\langle \Delta E \rangle$ on $\langle E \rangle$. By using this model we have, thus, been able to observe also in the case of CH_3F the same three distinct regions characterizing the dependence of τ_{VT} on $\langle E \rangle$ in SF_6 and CF_2HCl .^{1,4,5} However, we have also observed some differences which will be discussed upon further on. Finally, the results obtained with the above model will be discussed by making reference to the abundant experimental findings on the behaviour of τ_{VT} in medium size polyatomic molecules that we have gathered in the last few years.^{5,14-17}

2. THE KINETIC MODEL

According to NT scheme, we have considered the vibrational levels up to 4000 cm^{-1} (i.e. up to $4\nu_3$) and divided them into 14 distinct levels, including the ground state. The energies E_i , degeneracies, and numeration of these levels are given in *Table 1*.

Table 1 Vibrational energy levels of CH₃F taken into account in the kinetic model. Here $\nu_{25} \equiv (\nu_2, \nu_5)$ and $\nu_{125} \equiv (\nu_1, 2\nu_2, 2\nu_5, \nu_2 + \nu_5)$

Level number	Level	Energy (cm ⁻¹)	Degeneracy
1	ν_3	1049	1
2	ν_6	1182	2
3	ν_{25}	1466	3
4	$2\nu_3$	2081	1
5	$\nu_3 + \nu_6$	2230	2
6	$2\nu_6$	2348	3
7	$\nu_3 + \nu_{25}$	2634	6
8	ν_{125}	2914	7
9	ν_4	3009	2
10	$3\nu_3$	3098	1
11	$\nu_3 + \nu_{125}$	3963	7
12	$\nu_3 + \nu_4$	4058	2
13	$4\nu_3$	4099	1
14	0	0	1

Values for intramode and intermode rate of energy exchange are properly ascribed for these levels as shown in *Table 2*. The largest part of the rate values are deduced from experimentally measured quantities, another part is calculated from SSH theory, some of them were assigned with reasonable values¹². As revealed by LIF experiments, the V–T relaxation occurs primarily through the ν_3 and ν_6 modes which present the two lowest energy levels of the scheme. The ratio of the ν_3 to ν_6 V–T rate is assumed to be about 0.4 as calculated from the SSH theory.

The rate equations of the form

$$\frac{dN_i}{dt} = \text{intra(V-V)terms} + \text{inter(V-V)terms} + \text{(V-T)terms} \quad (1)$$

have been written for the populations of all the N_i levels. Since the rates for the intra and intermode exchange, as well as the rates for the V–T relaxation satisfy the principle of detailed balancing, only 13 ordinary differential equations are needed, the 14th being redundant.

For the explicit form of the equations of system (1) the interested reader is referred to Eq. (17–35) of the NT paper.¹² We have to mention however, some differences with respect to the NT model. Firstly, the excitation energy was not computed by assuming an absorption cross-section and a rotational relaxation rate, but by simply assuming that when the relaxation starts, the absorbed energy is found in the ν_3 ladder. This does not affect the relaxation modeling since we can neglect the population redistribution during the laser pulse. The fastest rate constant which characterizes the energy transfer from the ν_3 mode to other modes is estimated to be about $5 \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$, while for a standard CO₂ laser pulse with a time duration of about 100 nsec this value would be reached only at $p = 20$ torr. Therefore, at gas pressures of few torrs the assumption is justified. Such treatment gave us the possibility to study the dependence of the relaxation process not only on the average

Table 2 Energy transfer processes and rate constants used in the kinetic model. The rate constants for the backward reactions are calculated assuming the detailed balancing rule. The values of the rate constants are taken from Ref. 12 where the interested reader can find reference to the original works

Process	$\langle \Delta E \rangle$ (cm^{-1})	Rate constant $\times 10^{-5}$ ($\text{sec}^{-1} \times \text{torr}^{-1}$)
Intermode V-V energy transfer		
$v_3 + v_3 \rightarrow 2v_3 + (0)$	+17	$k_{U3} = 24$
$2v_3 + v_3 \rightarrow 3v_3 + (0)$	+32	$k_{U33} = 37$
$3v_3 + v_3 \rightarrow 4v_3 + (0)$	+48	$k_{U333} = 49$
$v_6 + v_6 \rightarrow 2v_6 + (0)$	+16	$k_{U6} = 10$
$v_{25} + v_{25} \rightarrow (v_{125} + (0))$	+18	$k_{U25} = 16$
$v_3 + v_6 \rightarrow (v_3 + v_6) + (0)$	+ 1	$k_{U36} = 10$
$v_3 + v_{25} \rightarrow (v_3 + v_{25}) + (0)$	0	$k_{U23} = 10$
$v_3 + v_{125} \rightarrow (v_3 + v_{125}) + (0)$	0	$k_{U13} = 10$
$v_6 + v_{25} \rightarrow (v_3 + v_{25}) + (0)$	+14	$k_{U26} = 10$
$v_3 + v_4 \rightarrow (v_3 + v_4) + (0)$	0	$k_{U34} = 10$
Intermode V-V energy transfer		
$v_3 + M \rightarrow v_6 + M$	-133	$k_{3,6} = 2.9$
$v_6 + M \rightarrow v_{25} + M$	-284	$k_{6,2} = 0.7$
$2v_3 + M \rightarrow (v_3 + v_6) + M$	-149	$k_{33,36} = 5.8$
$(v_3 + v_6) + M \rightarrow 2v_6 + M$	-118	$k_{36,66} = 5.8$
$2v_6 + M \rightarrow (v_6 + v_{25}) + M$	-286	$k_{66,26} = 1.4$
$(v_6 + v_{25}) + M \rightarrow v_{125} + M$	-280	$k_{26,1} = 1.4$
$(v_3 + v_6) + M \rightarrow (v_3 + v_{25}) + M$	-285	$k_{36,23} = 0.7$
$(v_3 + v_{25}) + M \rightarrow (v_6 + v_{25}) + M$	-119	$k_{23,26} = 2.9$
$3v_3 + M \rightarrow v_4 + M$	+ 89	$k_{333,4} = 5$
$nu_{125} + M \rightarrow v_4 - M$	- 95	$k_{1,4} = 10$
V-T/R energy transfer		
$nv_3 + M \rightarrow (n-1)v_3 + M$	+1049	$k_{r3} = 0.0037 \times n$
$nv_6 + M \rightarrow (n-1)v_6 + M$	+1182	$k_{r6} = 0.0087 \times n$

energy absorbed but also on the initial vibrational energy distribution for a fixed value of $\langle E \rangle$.

Secondly, since the aim of this paper is not to investigate intra- and inter-mode dynamics, the rate equations for all the levels were written and numerically integrated over a relatively long time interval (up to 2 msec) with an integration step of about 0.1 μs , in order to obtain the V-T characteristics. To this end, at each integration step we used the level populations $N_i(t)$ to compute the new vibrational energy

$$E(t) = \sum_{i=1}^{13} N_i(t) E_i \quad (2)$$

and, consequently, the new translational-rotational energy and translational temperature. We have also avoided to assign a common vibrational temperature to all the levels during the integration (see discussion below). At each step, appropriate corrections of the rate constants values were made in order to take into consideration their dependence on the translational temperature. Thirdly and finally, we have

rewritten Eq. (20) of ref. 12, which describes the dynamics of the $1\nu_3$ (N_i) level as follows:

$$\begin{aligned} \frac{dN_1}{dt} = & (4k_{t3}N_{14}N - 4k_{tb3}N_{11}N) + (3k_{tb3}N_4N - 3k_{t3}N_{11}N) \\ & + (k_{d333}N_{14}N_0 - k_{u333}N_{11}N_1) + (k_{u33}N_4N_1 - k_{d33}N_{11}N_0) \\ & + (k_{4,333}N_{10}N - k_{333,4}N_{11}N) \end{aligned}$$

with the notations used in *Table 2* for the rate constants, N being the total number of molecules in the unit volume.

The system of coupled differential equations was integrated numerically by a standard Runge-Kutta-Gill method. The time dependent vibrational energy $E(t)$ was used to compute both the instantaneous relaxation time

$$\tau_{VT}^{-1}(t) = \frac{d\{\ln[E(\infty) - E(t)]/E(\infty) - E(0)\}}{dt}, \quad (3)$$

and the so-called “effective” relaxation time τ_{eff} ,¹⁸ defined as the time in which the vibrational energy decays to the value:

$$E(\tau_{\text{eff}}) = [E(0) - E(\infty)]/e \quad (4)$$

In Eq. (3) and (4), $E(0)$ and $E(\infty)$ are the vibrational energies at time $t = 0$ (immediately after the laser pulse) and when the V-T/R equilibrium has been reached, respectively. Since we have not used a common vibrational temperature, all the quantities which characterize the equilibrium situation were computed before starting the integration, by using an iterative numerical method to balance the total energy between the degrees of freedom of the system. At the end of the integration we checked that the final value of each quantity is nearly equal to the corresponding equilibrium value.

The effective relaxation time yielded from each integration process has been used to compute the energy released per collision $\langle \Delta E \rangle$, according to the following expression

$$\langle \Delta E \rangle = \frac{\langle E \rangle}{p\tau_{\text{eff}}Z}, \quad (5)$$

where p and Z are the gas pressure and the rate of elastic collisions, respectively.

3. RESULTS AND DISCUSSIONS

All the results reported below refer to a pressure of 1 torr of pure CH_3F gas. The system (1) has been integrated for initial average vibrational energies (per molecule) ranging from 10 cm^{-1} to 3000 cm^{-1} . The result can be seen in Figure 1, where τ_{eff} is plotted as a function of $\langle E \rangle$. As one can see, after an initial plateau, the effective relaxation time strongly decreases by increasing the initial excitation energy, then reaches another plateau for energy values greater than about 1000 cm^{-1} . The same behaviour was observed experimentally for many small and intermediate size molecules: SF_6 ,⁴ CF_2HCl ,⁵ CS_2 ,⁶ and CF_2Cl_2 .¹⁴

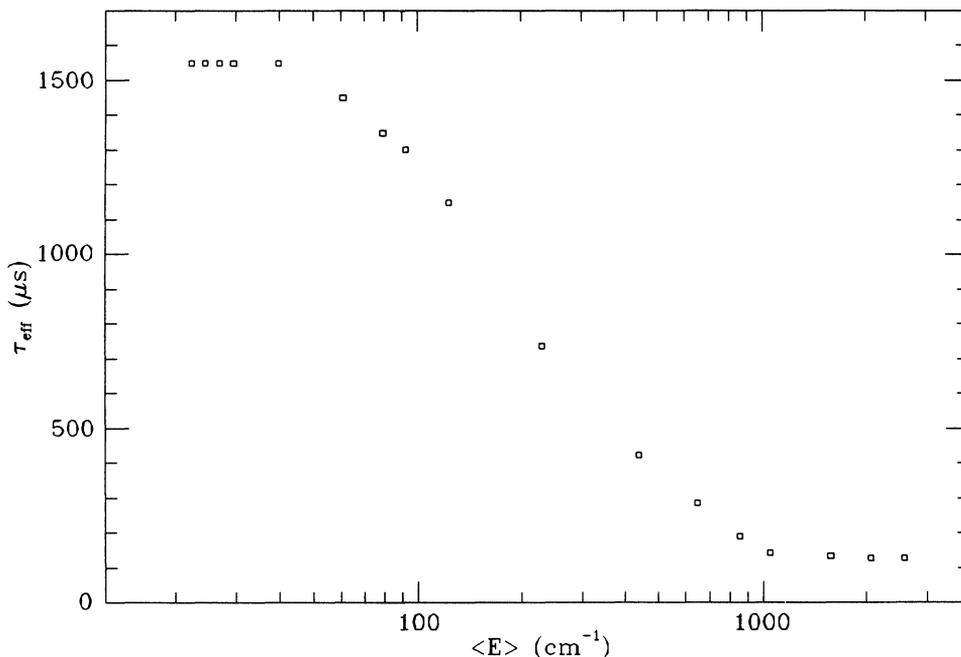


Figure 1 The dependence of the effective relaxation time (as defined by Eq. 4) on the energy absorbed per molecule. One can clearly observe the two plateaux corresponding to extremal excitation conditions.

We have also analysed the influence of the rate constants dependence on translational temperature, upon the relaxation time. We have firstly solved the equations of system (1) by using rate constants independent of temperature. Then, we have obtained a new solution by using the same initial conditions but recalculating at each integration step new rate constants, assuming a $T^{1/2}$ power law dependence. The two sets of results were almost identical in the low energy region (which is the expected result since, in this case, the gas does not heat up too much) and were only slightly different in the high energy range. Therefore, one may conclude that it is not the heating of the gas which causes the strong decrease of τ_{eff} , but the intrinsic nonlinearity of the relaxation process which is characteristic for high excited vibrational levels.

To illustrate this point we have plotted in Figure 2 the time dependence of the population of some vibrational levels, as governed by the rate equations for $\langle E \rangle = 500 \text{ cm}^{-1}$. Since we have used a semilogarithmic scale, the slope of each curve is proportional to the instantaneous V-T relaxation time of the corresponding level. It can be observed that during the relaxation the population of each level decays in a nonexponential manner, except perhaps the low levels ν_3 and ν_4 for which the effect is less pronounced. The fast rates observed in the first stage of the relaxation is due to the fact that a considerable amount of vibrational energy is transformed into kinetic energy during the V-V exchange processes. This effect has been observed experimen-

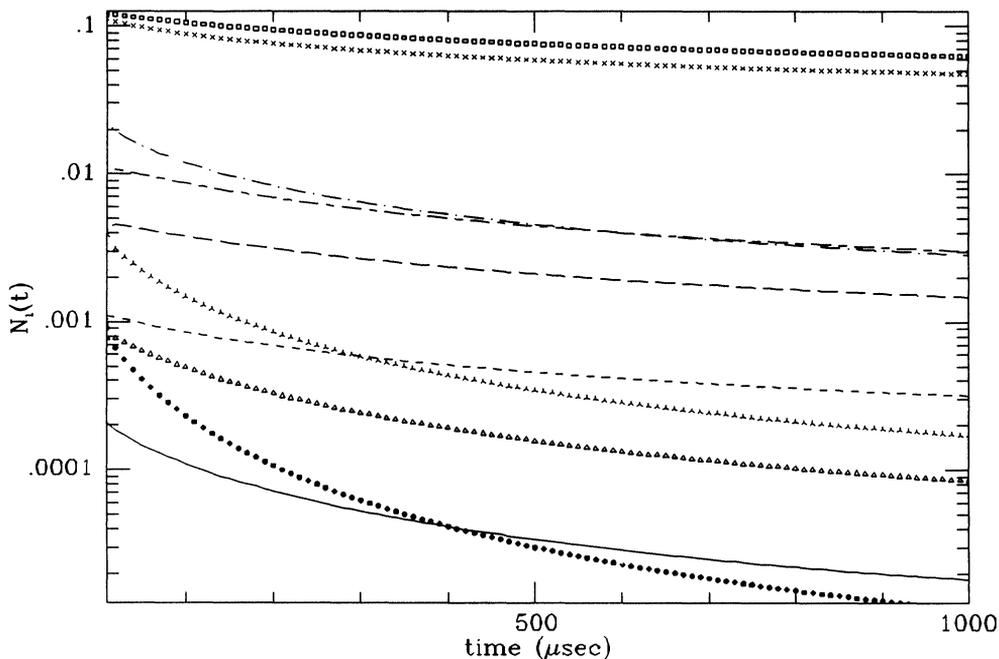


Figure 2 Time evolution of level populations for an initial excitation energy (E) = 500 cm^{-1} . The following levels are included: ν_3 : \times , ν_6 : \square , $2\nu_3$: $\cdots\cdots$, $\nu_5 + 2\nu_{25}$: — — — — , ν_4 : - - - - , $3\nu_3$: $\wedge \wedge$, $\nu_3 + \nu_{125}$: \triangle , $\nu_3 + \nu_4$: — — — — , $4\nu_3$: \bullet , ν_{25} : — — — — .

tally for molecules like CH_3Cl , $\text{CH}_3\text{Br}^{19}$ and CF_2HCl , which have the same number of atoms and similar spectroscopic structure. In addition one can see that the population ratio of certain levels is not constant. This means that the levels are not in equilibrium during the relaxation and, thus, one cannot define a common vibrational temperature to work with during the relaxation.

The nonlinear behaviour was also observed by Nakane and Tsukiya¹² and was attributed to the existence of the $3\nu_3 \leftrightarrow \nu_4$ V-V energy transfer which generates the so-called "catastrophic cyclic path" mechanism proposed by Mandich and Flynn²⁰ for explaining the nonlinear behaviour of the OCS vibrational relaxation. Briefly, the vibrational energy absorbed initially in the ν_3 ladder by single- or multi-photon processes has the tendency to accumulate into high lying levels by means of up-the-ladder collisions. The existence of the $3\nu_3 \leftrightarrow \nu_4$ V-V relaxation channel allows the vibrational energy to relax into lower vibrational levels of the other normal modes, a process which causes their repopulation, closes the cycle but also produces kinetic energy. In our opinion, the existence of the $3\nu_3 \leftrightarrow \nu_4$ coupling (which is questionable, as shown in¹²) is not essential for starting the catastrophic cyclic path described above. This is because in the high levels region the vibrational energy will always find a channel to transfer to other modes, thus starting the cycle which will produce the nonlinear V-T relaxation.

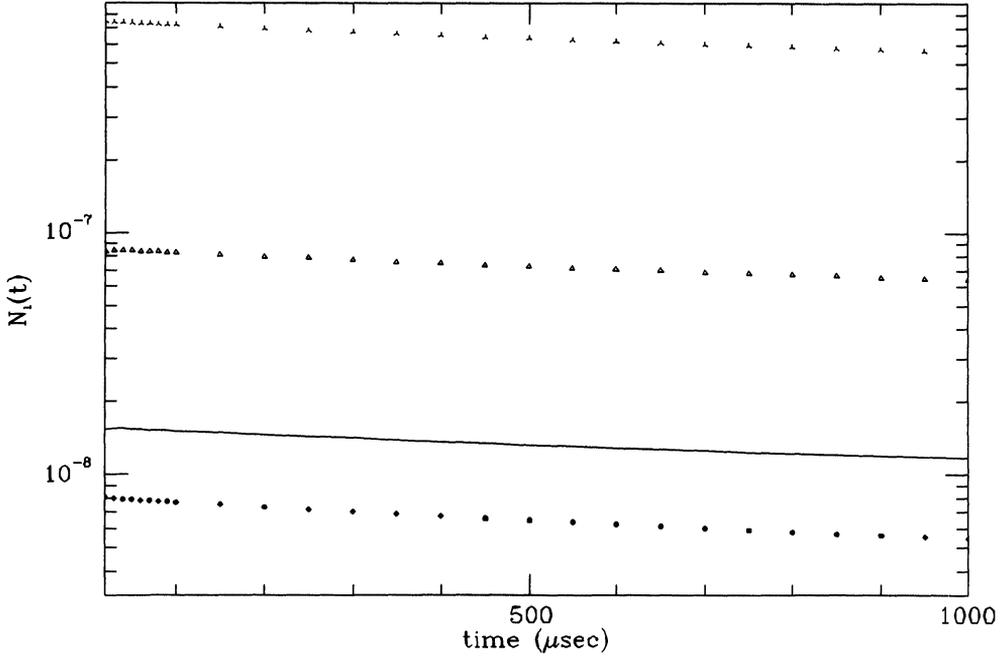


Figure 3 Same as in Figure 2 in the case of low excitation ($\langle E \rangle = 50 \text{ cm}^{-1}$), with the following levels included $3\nu_3$, $\nu_3 + \nu_{125}$, $\nu_3 + \nu_4$, $4\nu_3$, and with the same graphics as in Figure 2.

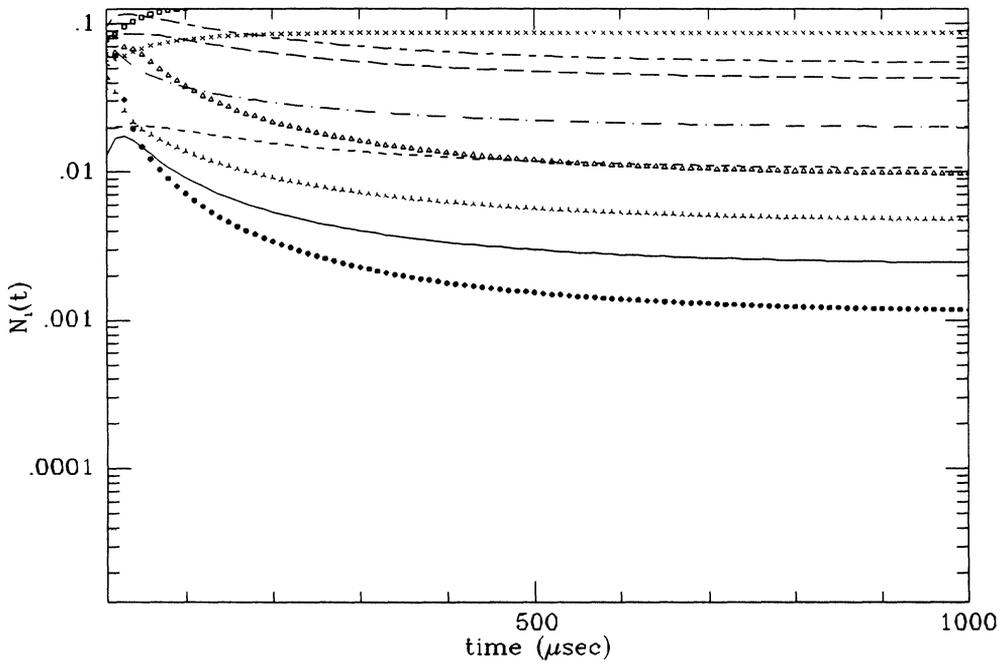


Figure 4 Same as in Figure 2 but with $\langle E \rangle = 2500 \text{ cm}^{-1}$.

On the contrary, in the case of weak excitation we have observed that the population distribution in all the levels is in equilibrium at any time during the relaxation, and that the single vibrational temperature decays exponentially. This is well evidenced in Figure 3 where the same level populations as in Figure 2 are represented for low initial excitation energy ($\langle E \rangle = 50 \text{ cm}^{-1}$ per molecule).

Finally, in order to get a better understanding of the dynamics of the level populations also in the case of intense molecular excitation, we have obtained a solution of system (1) for an energy value belonging to the region where a second plateau is observed in Figure 1, namely, $\langle E \rangle = 2500 \text{ cm}^{-1}$. We recall again that a relaxation time independent of the excitation energy corresponds to a regime of exponential decay of the vibrational energy. The results are stored in Figure 4, where the time evolution of the population of the same vibrational levels as in Figure 2 is reported.

Because of the initial strong non-equilibrium conditions, in the first stages of the vibrational relaxation the population of some of the levels decays in a non-exponential manner. However, at later times ($t \geq 200 \mu\text{s}$) all the population reach a quasi-equilibrium condition. This is contrary to what observed in Figure 2 ($\langle E \rangle = 500 \text{ cm}^{-1}$), where the nonlinear behaviour is evident at any time during the relaxation. Therefore, our results suggest that the exponential decay observed in CH_3F , as well as in other polyatomics, in the case of high excitation can be a

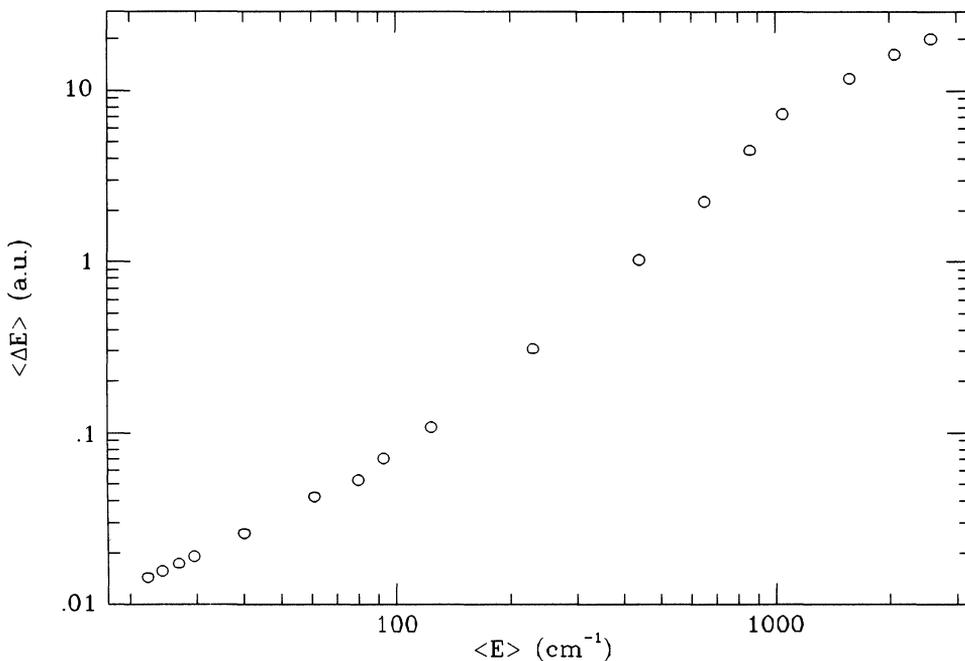


Figure 5 Log-Log plot of $\langle \Delta E \rangle$ as a function of $\langle E \rangle$. The calculated slopes of the curve are unity for extremal energy conditions and 2 for the intermediate region.

consequence of the fast initial redistribution of the energy among the highly excited levels, followed by a V-T relaxation with a common rate.

The energy released by collision $\langle \Delta E \rangle$ is represented in Figure 5 as a function of the energy absorbed per molecule $\langle E \rangle$ in a log-log plot. From this data we have calculated the power law dependences for the three distinct regions evidenced in Figure 1. We obtained a linear dependence

$$\Delta E \propto \langle E \rangle, \quad (6)$$

for the two plateaus, and a quadratic dependence

$$\Delta E \propto \langle E \rangle^2 \quad (7)$$

for the middle energy region. In fact one can verify from Figure 1 that τ_{eff} depends on $\langle E \rangle^{-1}$ in this last case. The same power laws were observed experimentally for CS₂.⁶

For CF₂HCl we observed linear dependences for extremal energy conditions (very high and very low excitations) and stronger than linear dependence for intermediate energy.⁵ The power index in this last case was found however to depend on the laser frequency used for the excitation. As mentioned in the Section II we have also studied the influence of the initial energy distribution on the relaxation time. For the case of CH₃F we have found very small differences in the instantaneous and effective relaxation times, when using the same initial amount of energy but stored in different levels of the ν_3 mode. This fact could be explained by the fact that, as seen in Table 2, the intra-mode V-V redistribution for the ν_3 mode is the fastest process in this molecule. In particular we observed that after few microseconds the level populations reach about the same values for equal excitation energies, independently on the initial distribution of this energy.

The fast ν_3 intermode V-V relaxation would explain also the unusually low threshold for which the decreasing of τ_{eff} occurs. As pointed out above, the τ_{eff} decreasing is produced when high lying levels begins to populate. Even in low fluence excitations, i.e. in the absence of multiphoton processes, these levels populate by the up-the-ladder type collisions, therefore compensating, at least partially, for the lack of multiphoton excitation.

4. CONCLUSIONS

We have carried out a theoretical analysis of the V-T relaxation process in CH₃F molecules. To this end we have used a modified version of a model originally developed by Nakane and Tsuchiya for studying V-V intra- and inter-molecular relaxation processes. Our study was mainly aimed to see whether a number of features characterizing the V-T relaxation in some important, intermediate size polyatomic molecules, such as SF₆, freons and related methylhalides, were still present in CH₃F. To this end, we have paid great attention on the V-T relaxation time dependence on $\langle E \rangle$. Our results have clearly evidenced (see Figure 1) that also

in CH_3F one can observe the same three different regions characterizing the dependence of τ_{VT} on $\langle E \rangle$ in other polyatomics, namely, a first initial plateau corresponding to low excitation energies followed by a region where the relaxation time strongly decreases, and, finally, a second plateau for energy values greater than about 1000 cm^{-1} .

This behaviour of τ_{VT} is the result of the different dynamical evolution of the population of the different vibrational levels in correspondence of different degrees of excitation. This is shown by the results of Figures 2–4, where we have reported the time dependence of the population of some vibrational levels for $\langle E \rangle = 50, 500$ and 2500 cm^{-1} , namely, values of $\langle E \rangle$ corresponding to the three regions previously discussed. While in the case of 50 cm^{-1} and 2500 cm^{-1} the decay of all the vibrational populations takes place in an exponential manner since the beginning ($\langle E \rangle = 50 \text{ cm}^{-1}$) of the relaxation, or after an initial, non-equilibrium stage ($\langle E \rangle = 2500 \text{ cm}^{-1}$), in the case of $\langle E \rangle = 500 \text{ cm}^{-1}$ the population of each level decays non-exponentially during all the relaxation process, and various vibrational levels are in a non-constant ratio.

We have also studied the influence of the initial energy distribution on the relaxation time. Our results show that only very small differences are observed in the instantaneous and effective relaxation times when the same total initial amount of energy is distributed in various manners among the levels of the infrared active ν_3 mode. This can be attributed to the fact that the intramode V–V rates for the ν_3 mode is the fastest process in CH_3F . We can, thus, conclude that the amount of energy transferred to the molecules and, as a consequence the level of excitation produced (up to the onset of the quasicontinuum), has more influence on the way the vibrational energy is relaxed, than the manner in which the same energy is distributed among the various modes. This has also been observed to be the case in other large polyatomic molecules.

Other two interesting aspects of our results are the very small influence that the dependence on the translational temperature of the rate constants used in the model bears upon the relaxation time, and the unusually low $\langle E \rangle$ value for which the decreasing of τ_{VT} occurs. This latter effect can be attributed to up-the-ladder type collisions that, given the fast ν_3 intermode V–V relaxation, can populate high lying vibrational levels even in a regime of low-fluence excitation of the molecules, i.e., in absence of multiphoton excitation. Finally, we have investigated the dependence of $\langle \Delta E \rangle$ on $\langle E \rangle$, again obtaining for CH_3F , results which confirm the experimental findings for other molecules like SF_6 ,⁴ CF_2HCl ,⁵ and CS_2 ,⁶ namely a linear dependence for extremal excitation energies, and a stronger than linear dependence for the middle energy region, where τ_{VT} shows to be dependent on $\langle E \rangle$.

In conclusion, although our study is obviously approximate and is not meant to provide precise, quantitative results for such a complex process as the vibrational relaxation in polyatomic molecules, nonetheless, it has made it possible to obtain interesting information for the CH_3F molecule by highlighting both features of the relaxation process which confirm what observed in other polyatomics, and new aspects which seem to characterize specifically the behaviour of CH_3F . We have recently undertaken an experimental analysis of the V–T relaxation process in CH_3F

aimed to testing the validity of our theoretical conclusions, and the final results will be the subject of a forthcoming publication.

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