

THE VIBRATIONAL–TRANSLATIONAL RELAXATION OF CF₂HCl in ARGON

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We report in this paper results concerning the vibrational–translational (VT) rates of CF₂HCl diluted in Ar as a neutral buffer. The dependence on the buffer concentration and on the initial vibrational energy distribution are obtained by using the 9R(48) and the 9R(34) CO₂ laser lines for the excitation process. The differences observed between the results corresponding to the two lines bear valuable information about the dependence of the VT relaxation process on the specific initial conditions of vibrational excitation.

KEY WORDS: Vibrational Energy Transfer, CO₂ laser excitation.

1. INTRODUCTION

The conversion of the vibrational energy in gas phase polyatomic molecules by vibrational–translational (VT) and vibrational–vibrational (VV) processes is important in many non-equilibrium chemical systems.¹ These fundamental processes occur in studying basic problems in inter- and intramolecular energy transfer as well as in laser-induced chemistry, pyrolysis, combustion, and atmospheric studies at high and low temperatures and pressures (see reference [2] for a general review concerning energy transfer in highly excited polyatomic molecules).

Typically most investigators have attacked this problem by examining the quenching efficiency for many different ‘cold’ gases (as He, Ar, CO, etc.) in relaxing a single ‘hot’ polyatomic by measuring the corresponding VT rates under a variety of experimental conditions.³ When the relaxation of an excited ensemble of molecules takes place in the presence of a buffer gas, the linear mixture rule (LMR) is almost invariably used in order to separate the effects of different collisional partners.⁴ For a binary mixture of X_g mole fraction of a relaxing molecular gas and X_b = 1 – X_g mole fraction of an inert buffer the LMR reads:

$$(p\tau_{VT})^{-1} = X_g (p\tau_{gg})^{-1} + X_b(p\tau_{gb})^{-1} \quad (1)$$

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where τ_{VT} , τ_{gg} , and τ_{gb} are respectively the relaxation times for the mixture, for the neat gas and for the gas infinitely diluted in the buffer, and p is the mixture total pressure.

The LMR is widely used for binary mixtures and it generally seems to work. Clearly, in the analysis of the relaxation processes in a gas mixture it is essential to know whether or not the LMR is valid, namely if the effects of different collision partners really can be added in this way. For example Barker and coworkers³ by studying the vibrational relaxation of highly excited toluene reported small deviations from the LMR for toluene-SF₆ mixtures while such deviations have been found to be significant in the toluene relaxation with other collider gases. Deviations from the LMR were also reported for other molecules: N₂O and CH₄,⁴ pentafluorobenzene (PFB),⁵ C₂H₂,⁶ and CF₂HCl,⁷ diluted in Ar. In such cases a generalisation of Eq. (1) taking the form⁶:

$$(p\tau_{VT})^{-n} = X_g(p\tau_{gg})^{-n} + X_b(p\tau_{gb})^{-n} \quad (2)$$

can be used to fit the data, in order to obtain $p\tau_{gb}$ for infinitely diluted gases. Here $n > 1$ is an additional fitting parameter which gives an estimate of the nonlinearity of the V-T process.

Our previous study⁷ concerning the vibrational relaxation of CF₂HCl in argon reported a strong deviation of this system from the LMR when a high laser fluence is used for the excitation of the molecule. On the contrary, for low laser fluence irradiations, the LMR was found to be fairly obeyed. The multiphoton absorption spectrum of this molecule⁸ indicated that, in the laser fluence range used by us, the laser field populated the high vibrational levels of the molecule. In this way we concluded that the violation of the LMR could be due to the population of the high lying vibrational levels during the excitation and to their subsequent involvement in the V-T relaxation.

Pure CF₂HCl relaxation was thoroughly studied by us.⁹ The calibration of the interferometric method allowed us to determine the dependence of the relaxation time on the average initial vibrational energy per molecule ($\langle\langle E \rangle\rangle$), for two different laser frequencies, namely 1086.86 cm⁻¹ (9R(34)) and 1093.85 cm⁻¹ (9R(48)). The differences observed in the relaxation time when the two laser frequencies produced the same $\langle\langle E \rangle\rangle$, led us to advance the hypothesis that the V-T relaxation is depending not only on the value of $\langle\langle E \rangle\rangle$ but also on the distribution of the total vibrational energy among the molecules of the ensemble.

We report in this paper some new results concerning the V-T relaxation rate of CF₂HCl diluted in Ar as a neutral buffer. We pay attention to the dependence of the V-T relaxation rate on the degree of Ar dilution, and on the extent and on the distribution of the initial vibrational excitation. In particular, the dependence of the V-T relaxation rate on the Ar mole fraction has been obtained for the above mentioned laser lines and at various laser fluences. Our results strongly support the idea that the initial vibrational energy distribution influences the V-T relaxation and confirm that measurements involving widely variable mixtures are capable of yielding more detailed information concerning specific vibrational-translational processes.

2. EXPERIMENTAL

A line tunable TEA CO₂ laser has been used for the vibrational excitation of the CF₂HCl gas. A stainless steel cell, 5 cm long and 10 cm i.d. equipped with KCl windows on both ends contained the gas mixture.

The V-T relaxation process of the excited molecules causes local heating and an expansion of the gas in a cylindrical symmetry. The consequent change in the gas density, and, thus, in the refractive index is sensed as a phase variation between the two arms of a Mach-Zehnder interferometer illuminated by a single mode, single frequency He-Ne laser. This experimental technique, named phase fluctuation optical heterodyne (PFLOH), has been described in detail elsewhere.^{10,11} Therefore, we shall only recall here some of its salient features.

In order to obtain a linear dependence of the signal on the refractive index variation, there are some restrictions imposed on the experimental parameters such as cell length, gas pressure, laser fluence. When proper conditions are met, the amplitude of the measured signal is proportional to the vibrational energy released by the molecules as kinetic energy. Thus, the signal temporal variation reflects the translational temperature variation in the sample and provides a determination of the corresponding relaxation time.^{8,9} We thoroughly analysed and discussed the capabilities of the method in References 8 and 11 to which the interested reader is referred for details.

All the measurements reported below have been carried out at 1 Torr total pressure, whatever the gas mixture used.

3. RESULTS

Assuming an exponential variation of the interferometric signal $V(t)$ we can write:

$$V(t) = V_0[1 - \exp(-t/\tau_{VT})] \quad (3)$$

where V_0 is the maximum amplitude. After acquisition, each signal is processed on an IBM-PC computer and the corresponding relaxation time τ_{VT} is found as the reciprocal of the slope of $\ln[1 - V(t)/V_0]$ plotted as a function of time. We mention that although the definition of τ_{VT} in Eq. (3) is somehow arbitrary for a nonexponential decay, it proved to be a useful tool in the description and characterisation of V-T relaxation processes (see references 7, 8, 9, and 11).

Typical temporal waveforms of the interferometric signals for the 9R(48) and 9R(34) laser lines are characterised by the same features (see, for example, those reported in reference 7): in CF₂HCl rich mixtures the signal is fairly exponential showing a well defined slope of the logarithmic signal, namely, a well resolved relaxation time. On the contrary, in Ar rich mixtures we have been able to measure only an average relaxation time since the interferometric signal proved to be non-exponential. We have observed both for 9R(34) and for 9R(48) laser lines a linear variation of the signal, and, therefore, a corresponding logarithmic curve yielding a

continuously variable slope. A similar behaviour was observed by Braun and Wallington⁵ for PFB in 70% Ar mole fraction. They reported an initial quasilinear portion in the translational energy–time curve which extended almost half-way through the translational relaxation process.

In general the errors in estimating the reported relaxation times from the above mentioned interferometric signals are of the order of 15% in Ar-rich mixtures, and of 10% in CF₂HCl-rich mixtures.

We have measured the V–T relaxation time for CF₂HCl + Ar mixtures varying from a pure relaxing gas to 90% Ar mole fraction. In this last case one can suppose that self-collisions (CF₂HCl*–CF₂HCl) although present, play a minor role in the V–T relaxation process. For both laser lines used in this experiment the relaxation times have been obtained in the same experimental conditions, namely 1 Torr total pressure.

The final goal of our investigation was to determine the behaviour of the relaxation rate when the two laser frequencies produced the same initial average vibrational energy. For this purpose we have used the data concerning the multiphoton absorption characteristics of CF₂HCl (see reference 8), and have irradiated the gas mixtures with appropriate laser fluences. For example, in order to obtain an average energy $\langle\langle E \rangle\rangle = 2000 \text{ cm}^{-1}$ one can deduce from [8] that the necessary laser fluences are 1.2 J/cm² and 1.5 J/cm² for the 9R(34) and 9R(48) laser lines, respectively.

We have represented the dependence of $(p\tau_{VT})^{-1}$ on the Ar mole fraction for two different values for the average vibrational energy absorbed per molecule: 700 cm⁻¹ (Figure 1) and 2000 cm⁻¹ (Figure 2). The 9R(48) results are plotted in Figure 1a and Figure 2a and the corresponding results for the 9R(34) line in Figure 1b and Figure 2b, for low and high content of initial vibrational energy, respectively.

As one can see from Figure 1 and Figure 2, the $(p\tau_{VT})^{-1}$ dependence on the Ar mole fraction exhibits different behaviours for different laser fluences and for different laser lines used for the vibrational excitations. However, in the case of low laser fluence, the V–T relaxation rates are not sensitive to the excitation frequency. Indeed from Figure 1 one can see that, in the limits of the experimental errors, the overall relaxation rates are practically the same for the two laser lines used for excitation for the whole range of Ar mole fraction values. This can be also appreciated by applying the nonlinear mixture rule, Eq. (2), to these low energy data. In fact, from a χ^2 best fit to our experimental data of Figures 1a and 1b we have obtained $n \approx 1.6$, with a confidence of about 25%, for both laser lines. The corresponding best fit curves are showed by the solid lines in both figures.

In the case of high vibrational excitation (Figure 2) the differences observed for the two laser lines are much more pronounced and cannot be interpreted as due to the experimental errors. The $(p\tau)^{-1}$ data corresponding to the 9R(34) line show a nonlinear behaviour: $(p\tau)^{-1}$ varies only mildly in CF₂HCl-rich mixture, while it changes more rapidly in Ar-rich mixtures. The corresponding data obtained for the 9R(48) line vary in the same numerical range as for the 9R(34) line but exhibit a linear decrease as the Ar mole fraction increases. In other terms, when the 9R(48) CO₂ laser line is used for excitation, the nonlinear behaviour in the V–T relaxation of CF₂HCl + Ar mixtures is either not present or is so small that cannot be evidenced

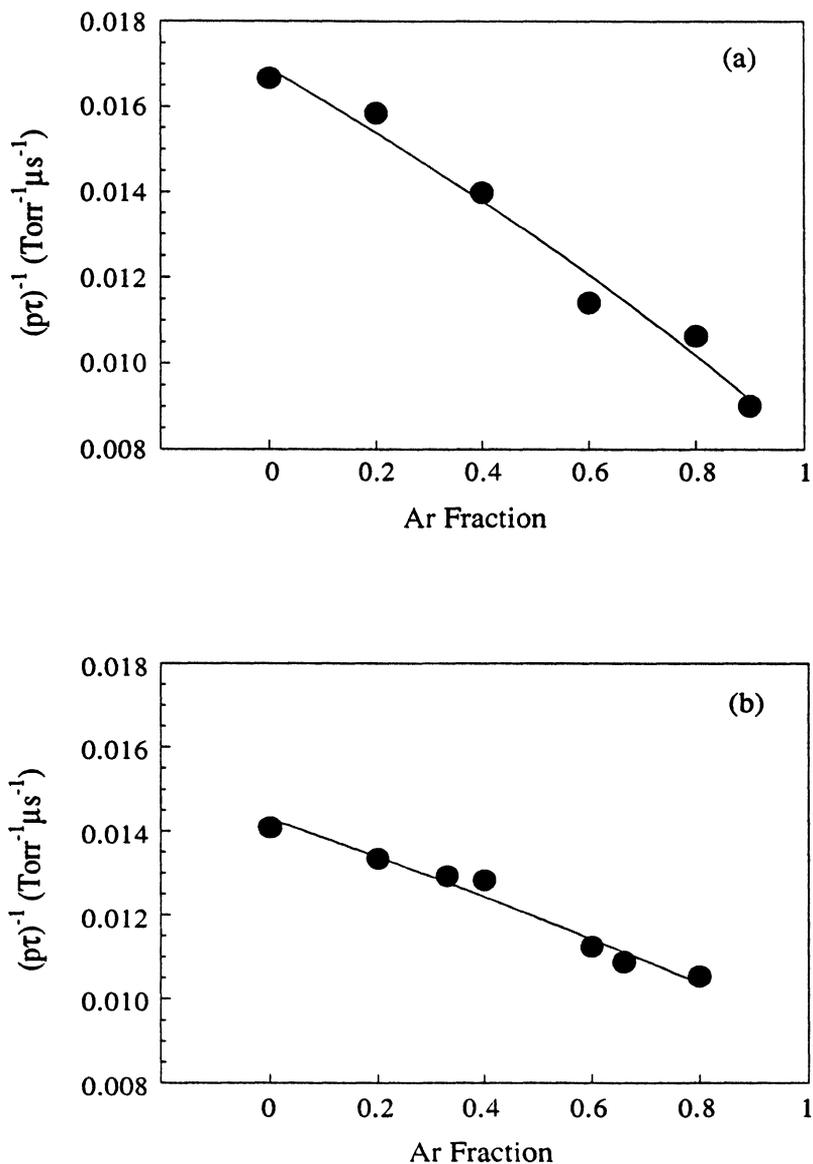


Figure 1 $(pt)^{-1}$ as a function of the Ar mole fraction for $\langle\langle E \rangle\rangle = 700 \text{ cm}^{-1}$. (a): 9R(48) laser line; (b): 9R(34) laser line. The total gas pressure is 1 Torr. In both cases the solid lines through the experimental points represent χ^2 best fits obtained from Eq. 2 with $n \approx 1.6$.

by the interferometric method. The differences between these data are also evident when Eq. (2) is again applied for a χ^2 fit. While the 9R(48) data yield a value for n close to unity, the corresponding 9R(34) data yield $n \approx 3$. As in Figure 1 the solid lines through the experimental points represent the relative best-fit curves. It is worth

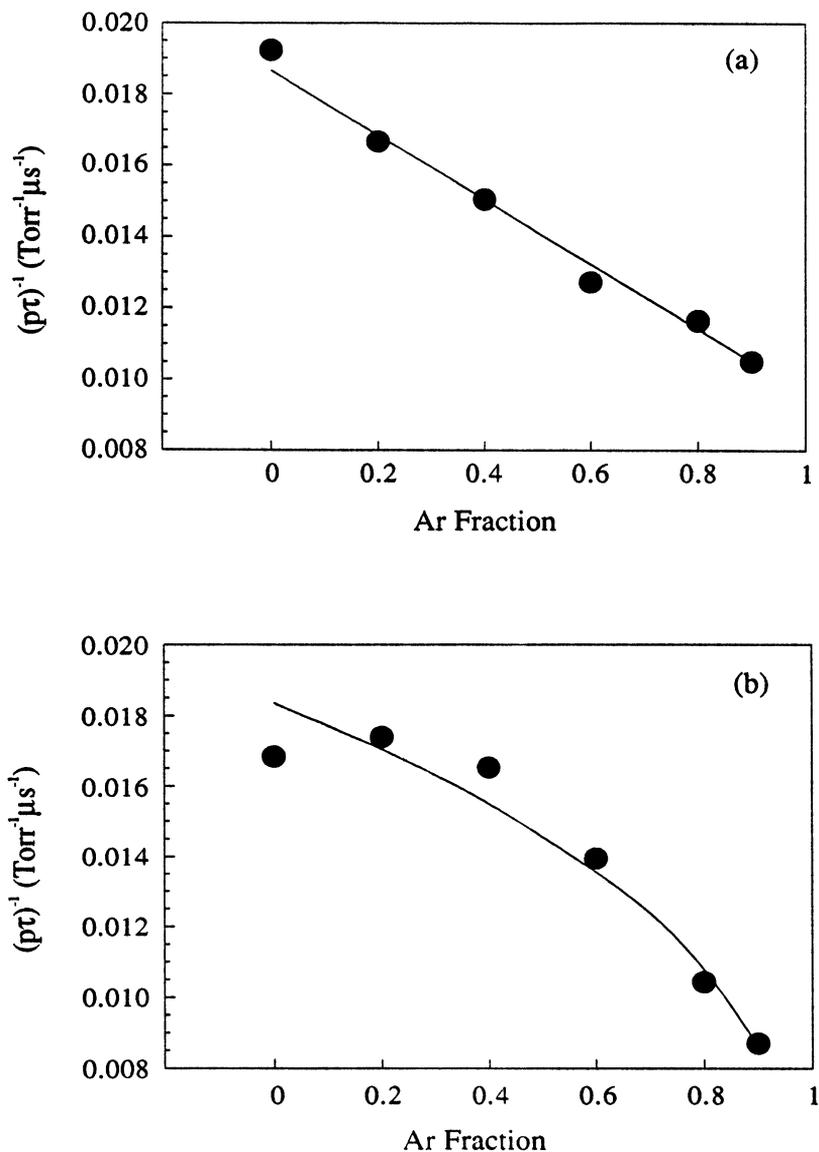


Figure 2 $(p\tau)^{-1}$ as a function of the Ar mole fraction for $\langle\langle E \rangle\rangle = 2000 \text{ cm}^{-1}$. (a): 9R(48) laser line; (b): 9R(34) line. The total gas pressure is 1 Torr. The χ^2 best fits from Eq. 2 have been obtained for $n \approx 1$ (case a) and $n \approx 3$ (case b).

noting that as the vibrational excitation energy increases so does the nonlinearity of the relaxation data for the 9R(34) line. In other words, the deviation from the LMR becomes more and more pronounced. Previous data reported by us⁷ for a laser fluence of about 1.9 J/cm^2 , which corresponds to an average excitation energy $\langle\langle E \rangle\rangle = 3000 \text{ cm}^{-1}$, yielded $n = 4.6$ for the nonlinear mixture rule fit.

4. DISCUSSION AND CONCLUSION

At present, no theoretical models are available which can provide a quantitative description of energy transfer in highly excited polyatomic molecules, although several models can give qualitative agreement or can be adjusted to fit experimental data. To make progress towards a complete understanding of large-molecule energy transfer the experimental conditions have to be selected so as to investigate specific aspects of the problem.

The fundamental motivation of the present investigation was to establish whether or not the specific conditions of vibrational excitations had some influence on the molecular V-T relaxation process. We reported in reference 9 for neat CF₂HCl a first experimental evidence supporting this hypothesis. In that case we demonstrated that different laser frequencies, although producing the same value of $\langle\langle E \rangle\rangle$, led to different relaxation rates.

Our present results provide additional evidence to the circumstance that the V-T relaxation time depends not only on the amount of initial average vibrational energy, but also on the way this energy is distributed among the various molecules of the gas sample.

It is well known that at high laser fluences the vibrational energy distribution can be essentially considered bimodal.¹² Just after the exciting laser pulse ceases there are mainly two ensembles of excited molecules: the "hot ensemble" including molecules with an average vibrational energy, statistically distributed over all modes, above the threshold of the "quasicontinuum" (QC); and the "warm ensemble" including molecules for which the energy of nonresonant vibrational modes correspond to that of room temperature while the energy of the excited mode (ν_3 for CF₂HCl) is higher, but not exceeding a few quanta (1-3). There is, obviously, a third ensemble of unexcited molecules ("cold ensemble").

It has also been experimentally demonstrated⁹ that different laser frequencies can generate different bimodal distributions for a given value of $\langle\langle E \rangle\rangle$. For example, in our case at high laser fluences the more red-shifted (with respect to the $\nu_3 = 1100$ cm⁻¹ fundamental of CF₂HCl) 9R(34) laser line will produce, through three- and four-photon resonances (see the CF₂HCl multiphoton absorption spectra of reference 8), more "hot" than "warm" molecules. On the contrary, at the same laser fluence, the 9R(48) laser line which is more resonant to the ν_3 fundamental will mainly excite the molecules into the first and second vibrational levels of this mode, thus populating preferentially the "warm ensemble".

It is not clear whether or not the initial energy distribution is destroyed by the fast intra- and intermolecular VV relaxation. However, our investigation provides experimental evidence that seems to enforce the hypothesis that the bimodal character ("hot" and "warm") of the distribution, as well as the initial ratio between the two ensembles are conserved, at least partially.

In our experiment at low excitation energies both laser frequencies have led to a condition where the LMR is fairly well obeyed (see Figures 1a and 1b). In this case the "hot ensemble" is practically empty and the V-T relaxation process involves only low lying, discrete vibrational levels of the fundamental ν_3 mode. This is the

condition where the relaxation rates of each collision partners (molecule–molecule and molecule–buffer) can be linearly added to give the overall V–T relaxation rate, i.e., the LMR is fairly well satisfied.

On the contrary, at high excitation energies (Figures 2a and 2b) the features of the V–T relaxation process corresponding to different laser lines are markedly different. This reflects the difference in the initial vibrational energy distributions in the two cases. At a given average vibrational energy ($\langle\langle E \rangle\rangle = 2000 \text{ cm}^{-1}$, in our case), according to the above discussion one can say that the 9R(48) laser line will preferentially excite a higher number of molecules (with respect to the 9R(34) line) but in the “warm ensemble”. Thus, this ensemble will be predominant during the relaxation process, and our data (Figure 2a) show that, again, the LMR is fairly well satisfied. On the other hand, Figure 2b shows that when the 9R(34) line is used in the excitation step and, as a consequence, the same average vibrational energy (2000 cm^{-1}) is mainly distributed among fewer but “hotter” (with respect to the 9R(48) line) molecules, the departure from the LMR is evident and considerably strong.

It is worth mentioning that a behaviour very similar to that of Figure 2b was also reported by Braun and Wallington⁵ for PFB in Argon. Our present explanation of the relaxation process of CF_2HCl in Argon is mainly based on a qualitative analysis. Nonetheless, the features of the results of the present paper confirm what we observed for neat CF_2HCl , thus supporting the hypothesis of a strong influence of the initial energy distribution on the subsequent V–T relaxation process.

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