

Features in the vibrational relaxation of laser excited Freon-22 molecules

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Abstract. The vibration–translation (V–T) of laser excited Freon-22 (CF₂HCl) molecules has been studied. An interferometric technique allows simultaneous measurement of the initial energy $\langle E \rangle$ stored in the molecules, and of the V–T relaxation time. Consequently, the V–T relaxation time and the energy released per collision can be determined as a function of the energy absorbed from the laser field. Three distinct regions have been observed for these dependences. This behaviour observed and reported by us for Freon-22 confirms the role played in the relaxation process by the initial distribution of the vibrational energy, and agrees qualitatively with the experimental results for other polyatomic molecules.

Keywords. Laser excitation; vibrational relaxation; polyatomic molecules.

1. Introduction

In the last period, a number of papers have 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 like tetra- and hexafluorides, fluorochloromethanes, etc (see Gordon 1988, 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 the molecule. We must mention the results obtained by Troe and coworkers (see Hippler and Troe 1989, and references cited therein) on a large class of molecules ranging from triatomics (where an E^2 has been observed for intermediate energies and a linear dependence for higher energies) up to large polyatomics (where a transition from linear to nearly independent $\langle \Delta E \rangle$ or $\langle \Delta E \rangle$ has been detected as excitation energy increases).

For one of the most intensively studied molecules, namely SF₆, has been found (Lenzi *et al* 1986; Braun *et al* 1987; Beck and Gordon 1988) a linear dependence of $\langle \Delta E \rangle$ on $\langle E \rangle$ for high excitation energies, and stronger than linear (3/2 power index) for values of $\langle E \rangle$ which correspond to the sparse region of vibrational levels. However it should be pointed out that Braun *et al* (1988) and Steinfeld *et al* (1970) found a linear dependence also for very low excitation energies (up to 1000 cm⁻¹). Often the results are a source of controversy and the dynamical factors governing this dependence are still under investigation both experimentally and theoretically.

Bearing in mind these observations, and aiming for better understanding of the roles played by the sparse and the quasicontinuum (QC) energy regions, we examined

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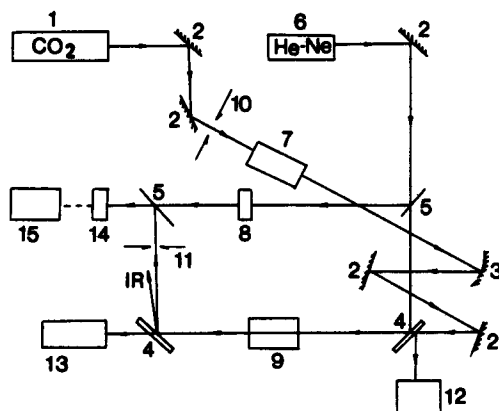


Figure 1. The experimental set-up used in the PFLOH method. (1) – CO₂ laser, (2), (3) – mirrors, (4) – Ge windows, (5) – beam splitters, (6) – HeNe laser, (7) – absorbing gas for fluence regulation, (8) – Babinet-Soleil phase compensator, (12) – energimeter, (13) – frequency analyser.

the vibration–translation relaxation of CF₂HCl both as a function of the vibrational energy and as a function of its initial distribution created by two different laser lines.

2. Experimental technique

We used the phase fluctuation optical heterodyne (PFLOH) technique (Davis and Petuchovski 1981) in an experimental set-up shown schematically in figure 1. It has been described in detail by Tosa *et al* (1989) together with the calibration method used and thus we shall only mention here that the method allows the simultaneous measurement (Bruzzese *et al* 1989) of the energy absorbed and of the effective relaxation time. A gas cell (9) is placed in one arm of a Mach-Zender interferometer illuminated by a linearly polarized single mode HeNe laser (6). The excitation laser (1) is a line tunable TEA CO₂ laser delivering up to 5 J/pulse (100 ns FWHM, with a long tail of about 1 μs containing less than 20% of the total pulse energy) on each line. Both CO₂ and HeNe beams overlap in the sample zone, with the CO₂ laser inducing the refractive index change and the HeNe laser beam probing it. A photodiode (14) detects the heterodyne signal, which is then fed into a storage oscilloscope (15) and then into a computer for the final analysis. All the experiments were carried out at room temperature and with gas pressures ranging from 0.5 to 5 torr. Only results concerning neat (99.8% purity) CF₂HCl are reported here. No buffer gas was added.

3. Results and conclusions

Two typical sets of τ_{eff} vs. $\langle E \rangle$ for $p = 2$ torr are presented in figure 2. The two curves have been obtained by using the 9R(8) and 9R(48) CO₂ laser lines. One can clearly observe an initial plateau in the low energy region, followed by a domain of rather abrupt decrease. The occurrence of a second plateau is evident only for 9R(48) data

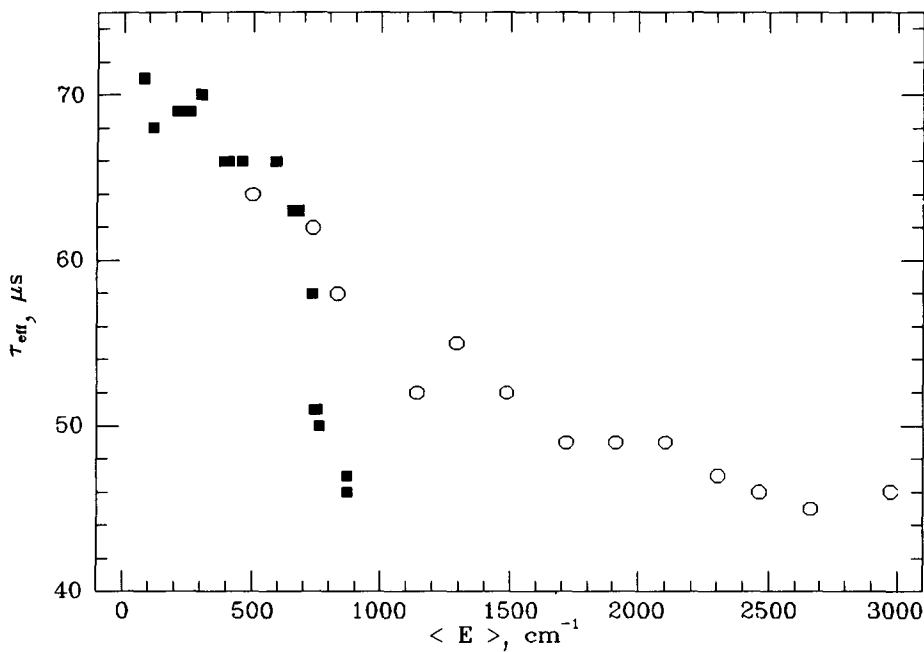


Figure 2. The dependence of the effective V-T relaxation time on $\langle E \rangle$ the energy absorbed by the molecules from the laser field, for 9R(8) (■) and 9R(48) (○) CO₂ laser lines.

since for the laser fluence used in the experiments, the less absorbing 9R(8) line is not able to produce enough vibrational energy to reach the plateau.

The energy released per collision can be computed from the above data according to the relation:

$$\langle \Delta E \rangle = \frac{\langle E \rangle}{R\tau_{\text{eff}}Z}, \quad (1)$$

where Z is the rigid sphere collision rate at p Torr. The results for Freon-22 and the two laser lines used are plotted in figure 3. The linear dependence observed for low $\langle E \rangle$ values, corresponds to constant VT relaxation time. Indeed, a least squares fit performed for different energy regions for $R(8)$ and $R(48)$ lines, give the values listed in table 1. Also listed in table 1 are the values for an intermediate CO₂ laser frequency namely $R(34)$ previously reported by Tosa *et al* 1989.

The differences observed in the relaxation behaviour when different laser frequencies are used for the excitation might be put in correspondence with the initial distribution of the vibrationally excited molecules. In particular, $R(8)$, which is more red-shifted with respect to the ν_3 fundamental, produces a smaller fraction of excited molecules but at a higher level of excitation, while $R(48)$, which is closer to the CF₂HCl ν_3 fundamental, excites a larger fraction of molecules though at a lower level of excitation. It is not clear whether this initial distribution is destroyed or partially destroyed by the fast intra- and intermolecular V-V relaxation. However it is clear that, when the V-T "clock" starts, the molecules are found in three main groups: unexcited ("cold") molecules, "warm" molecules which have the average vibrational energy below the

Table 1. Power dependencies of $\langle \Delta E \rangle$ on $\langle E \rangle$ for $R(8)$, $R(34)$ and $R(48)$ laser lines and different energy regions.

Laser line	Energy region (cm^{-1})	Power index
$R(8)$	100–500	1.03
$R(8)$	500–1000	2.35
$R(34)$	500–900	1.01
$R(34)$	900–2000	1.36
$R(48)$	900–2000	1.24
$R(48)$	2000–3000	1.05

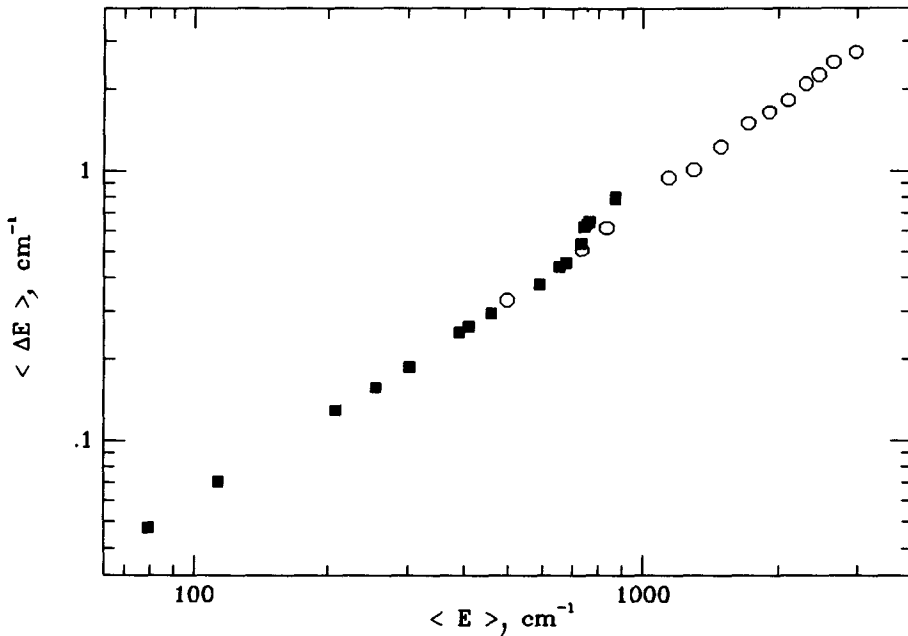


Figure 3. The dependence of the energy released per collision $\langle \Delta E \rangle$ on $\langle E \rangle$, for 9R(8) (■) and 9R(48) (○) CO_2 laser lines.

limit for starting the QC, and finally, “hot” molecules with the average vibrational energy above this limit. The amounts of these three types of molecules and their ratios depend obviously on the initial vibrational distribution. Moreover, it has been proved (Gordon 1988) that a sizable amount of energy is converted into translation during the V–V process and thus the initial vibrational distribution could influence the V–T relaxation process.

Finally we mention that in order to assess the relative importance of the above described mechanisms we have developed (see Tosa *et al* 1989) a very simple three-level model which is able to explain the main qualitative features of the results presented above and to which the interested reader is referred.

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