NOTIZEN

Vibrational Energy Transfer in CHF_3-Mixtures

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The vibrational relaxation times for pure CHF_3 and CHF_3 diluted in H_2, D_2, Ar, Kr and Xe are 0.55; 0.01, 0.025, 2.6, 4.8, and 5.6 μsec atm at 298 K. These measurements complete previous results obtained for the systems CHF_3-He, Ne, Ar. Correlation of the rare-gas results according to SSH-theory shows that relatively small rotational contributions may be expected for the heavy collision partners Kr and Xe.

1. Introduction

The transfer of energy between vibrational, rotational and translational degrees of freedom is of fundamental importance for an understanding of many processes. The new fields of laser-induced chemical reactions and isotope separation, for example, need detailed information about energy transfer. To describe the energy flow from vibrational degrees of freedom to rotational and translational degrees of freedom sophisticated V-T models and crude V-R models are available. However, many papers published in recent years point out that an integrated V-R, T theory is necessary to describe the experimental results. For example, the vibrational relaxation in some rare-gas mixtures of CF_4 [1], CH_2F_2 [2], and CH_3F [3] is affected by vibration-rotation interaction. The extensive data available now for rare-gas mixtures of CF_4, CHF_3, CH_2F_2 and CH_3F can help to come to a better understanding of V-R, T processes and to test new V-R, T models.

2. Experimental Results

In this note we report vibrational relaxation times for CHF_3 diluted in H_2, D_2, Ar, Kr, and Xe. The following Messer-Griesheim research-grade gases were used without further purification: CHF_3 DIN 8960; H_2 99.999%; D_2 99.7%; Ar 99.997%; Kr 99.99%; and Xe 99.99%.

The measurements have been performed at 298 K using an ultrasonic absorption apparatus working in the region 30 kHz/atm – 6 MHz/atm as described elsewhere [4]. The results are shown in Table I together with the already known relaxation times for CHF_3-He, Ne determined by dispersion measurements [5]. Our values for the self-relaxation of CHF_3 and for the system CHF_3-Ar are in close agreement with the corresponding relaxation times $p\tau = 0.556$ μsec atm and $p\tau = 2.33$ μsec atm given in Reference [5]. The relaxation times $p\tau = 0.608$ μsec atm [6] and $p\tau = 0.474$ μsec atm [7] for the self-relaxation of CHF_3 at 298 K, and 300 K respectively, are within the error of our value.

Table I. Relaxation times and transition probabilities for pure CHF_3 and CHF_3 mixtures.

	$p\tau$ [μsec atm]		$\sigma_{CHF_3\text{-}X}$ [b] [Å]	P $[P=(Z\tau)^{-1}]$ [d]	L [Å]
CHF_3-CHF_3	0.55	±0.1	4.2 [c]	$3.1\cdot10^{-4}$	0.24
CHF_3-H_2	0.01	±0.006	3.57	$5.7\cdot10^{-3}$	0.204
CHF_3-D_2	0.025	±0.015	3.57	$3.2\cdot10^{-3}$	0.204
CHF_3-He	0.0578	±0.005 [a]	3.39	$1.5\cdot10^{-3}$	0.194
CHF_3-Ne	0.813	±0.045 [a]	3.53	$2.0\cdot10^{-4}$	0.202
CHF_3-Ar	2.6	±0.8	3.83	$6.8\cdot10^{-5}$	0.219
CHF_3-Kr	4.8	±1.5	3.91	$4.3\cdot10^{-5}$	0.223
CHF_3-Xe	5.6	±1.7	4.13	$3.6\cdot10^{-5}$	0.236

[a] Ref. [5]. [b] $\sigma_{CHF_3\text{-}X} = (\sigma_{CHF_3} + \sigma_X)/2$ with σ_X from Ref. [9].
[c] Ref. [8]. [d] $Z = 2N\sigma^2(2\pi RT/\mu)^{1/2}$.

The results for the collision partners H_2 and D_2 are less accurate, because in these systems only mixtures with low concentrations (H_2, $D_2 \leqq 10\%$) could be investigated. The reason for this limitation was the high deactivation probability of these gases which causes a shift of the absorption maximum out of the region measurable with our apparatus at high hydrogen concentrations.

The transition probabilities shown in Table I have been calculated using the rigid-sphere expression to determine the gas-kinetic collision number Z and the collision diameters given in Table I.

3. Discussion and Conclusions

The following conclusions may be obtained from the results for the CHF_3 mixtures:

1. Deuterium is about two times as effective as Helium, although they have the same mass. Hydrogen also seems to be more effective than a hypothetical atomic collision partner of the same mass. These higher transition probabilities of the diatomic collision partners can be explained by additional relaxation channels available in these molecules.

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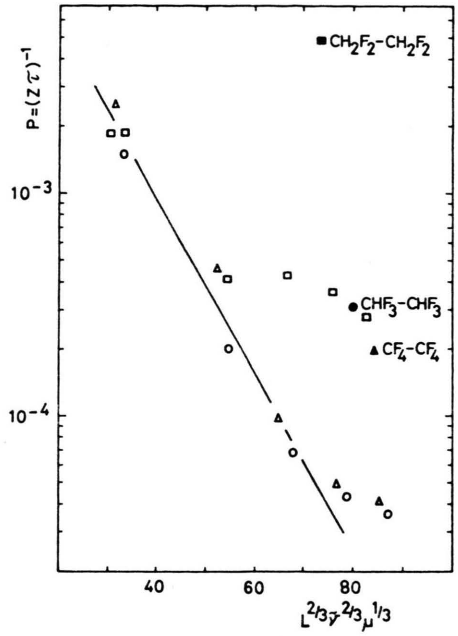

Fig. 1. Transition probabilities versus $L^{2/3}\,\tilde{\nu}^{2/3}\,\mu^{1/3}$ [$Å^{2/3}$ $cm^{-2/3}$ $amu^{1/3}$]: □ CH_2F_2-^3He, ^4He, Ne, Ar, Kr, Xe, ■ CH_2F_2-CH_2F_2 [2]; ○ CHF_3-^4He, Ne, Ar, Kr, Xe, ● CHF_3-CHF_3, this work and Ref. [5]; △ CF_4-^4He, Ne, Ar, Kr, Xe, ▲ CF_4-CF_4 [1].

2. The transition probability for the self-relaxation of CHF_3 is about seven times higher than the value expected for a hypothetical atom of the same mass.

3. The corresponding rare-gas mixtures of CHF_3 and CF_4 have similar transition probabilities. This is true for the systems CH_2F_2-He, Ne also; the transition probabilities for the heavy collision partners Ar, Kr and Xe however, deviate appreciably (see Figure 1).

To determine deviations from a simple V-T model usually the transition probability is plotted versus $\mu^{1/3}$, where μ is the reduced mass of the collision partners. In such a plot for the CHF_3 rare-gas systems the value for CHF_3-He does not fit the curve connecting the other points. A similar effect has been found for the corresponding CF_4 systems (see Fig. 3 of Reference [1]). This discontinuity disappears completely for the CHF_3 systems and partially for the CF_4 systems, if we take into consideration that the potential energy parameter "L" is not constant for the different rare-gas systems. Unfortunately, no experimental values are available. Therefore, we used the general approximate formula $L \approx \sigma/17.5$ to calculate the L-values from the corresponding collision diameters [10].

This procedure is qualitative at best. The values obtained for the potential parameters of the CHF_3 mixtures are shown in the last column of Table I.

In Fig. 1 the transition probabilities for the rare-gas mixtures of CH_2F_2, CHF_3, and CF_4 are plotted according to SSH-theory. These three polyatomic molecules have similar wave numbers for the relaxing C–F bending modes namely, 529 cm^{-1}, 507 cm^{-1}, and 435 cm^{-1}. However, the smallest moment of inertia changes considerably: CH_2F_2: $I=10.3$ amu $Å^2$; CHF_3: $I=48.8$ amu $Å^2$; and CF_4: $I=87.8$ amu $Å^2$. Therefore, we expect decreasing rotational contributions from CH_2F_2 to CF_4 according to simple V-R models. Figure 1 shows clearly that large deviations from the expected straight line occur for Ar, Kr, and Xe in collisions with CH_2F_2. However, for the molecules CHF_3 and CF_4 which possess relatively high moments of inertia only the Xe-values deviate considerably. The self-relaxation also should be influenced by the different moments of inertia. In fact, we see that the ratio of the experimental transition probability to the value expected according to the straight line of Fig. 1 is about 100 for CH_2F_2 and about 10 for CHF_3 and CF_4. Thus, the results for the self-relaxation may be interpreted qualitatively by the V-R model. However, the departures from linearity can be influenced by other collision parameters also. Boade, for example, comes to the conclusion that the relaxation in pure CF_4 and CHF_3 is in accordance with SSH theory [11] by estimating the L-values in a different manner.

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