Low Temperature Vibrational Relaxation of Gaseous CF_3Cl, CF_3Br, CHF_2Cl, and CH_3Cl

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Ultrasonic absorption measurements are reported for gaseous CF_3Cl, CF_3Br, CHF_2Cl, and CH_3Cl between room temperature and the lower temperatures 163 K, 193 K, 198 K, and 213 K, respectively. Starting from a statistical point of view, the relaxation behavior is divided into three classes, which are associated with the positive, zero, and negative slope in a $\log(k)$ versus $1/T$ plot. On this basis the vibrational relaxation behavior of CF_4, CF_3Cl, CF_3Br, CHF_3, CHF_2Cl, CH_3Cl, NF_3, PF_3, and BF_3 is discussed especially in the critical temperature to boiling point region. This temperature region is used as a reference for comparing different molecules.

Introduction

Our knowledge of vibrational relaxation in diatomic and polyatomic molecules has increased rapidly in recent years [1], [2]. The development of laser techniques makes a systematic investigation of $V-V$ processes possible [2]. Acoustic methods are important to study $V-R, T$ transfer, especially in polyatomic molecules with low lying vibrational levels [1]. Sound absorption measurements are also used to study vibrational relaxation at very low frequency/pressure ratios [3].

The theoretical treatment of inelastic collisions has a long tradition. First studies were already performed in the years quantum mechanics was developed. Despite continuous effort, solutions could only be found for relatively simple model systems. Thus the experimental data of polyatomic molecules are still discussed in terms of simple relaxation models. The purpose of such models is not a quantitative description of the data, but to gain an understanding of the essential features and molecular properties which govern the inelastic collision processes. Good models give physical insight; however, the application is limited to a certain temperature and pressure range which changes from compound to compound.

At low pressures and at temperatures far above the critical point, the attractive part and the anisotropy of the intermolecular potential play a minor role in $V-R, T$ transfer processes, where normally a relatively large energy quantum is involved. This is the reason for the success of the simple Landau-Teller model (where only repulsive forces and central collisions are taken into account) and of the refined theories, such as SSH-theory, based on this concept [4]. Below the critical temperature these simplifications are no longer allowed and the molecule-specific intermolecular potential produces an increasing individualism of the relaxation behavior. Therefore, no general law for the temperature dependence of the rate constants has been found in this region.

Below room temperature vibrational relaxation has been studied for a relatively small number of polyatomic molecules. In this work experimental results are reported for CF_3Cl, CF_3Br, CHF_2Cl, and CH_3Cl, extending the investigated temperature range below the boiling point of these substances. A general discussion of the temperature dependence of the rate constant is given, adopting a statistical point of view. In this discussion prior results obtained for CF_4, CHF_3, NF_3, PF_3, and BF_3 are included.

Experimental

The apparatus used for the ultrasonic absorption measurements has been described in detail elsewhere [5]. Information on the condenser-type sound transducers, developed for the low temperature experiments, may be found in [6]. Measurements were performed between room temperature and 163 K, 193 K, 198 K, and 213 K for CF_3Cl, CF_3Br, CHF_2Cl, and CH_3Cl, respectively. Thereby, results

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are now available for these molecules from above the critical temperature to below the boiling point. The extension to even lower temperatures was limited by the vapor pressure of the compounds.

The CF_3Cl and CF_3Br samples were supplied by Matheson and had a purity of 99.0%. CHF_2Cl and CH_3Cl were delivered by Baker and had a stated purity of 99.9% and 99.5%, respectively. Before use, all gases were further purified. The samples were repeatedly cooled to 77 K and non-condensable impurities were removed by pumping.

Results

All experimental results are collected in Table 1. For the four gases studied, the temperatures, the corresponding frequency/pressure ratios of maximum molecular absorption $(\nu/p)_{\max}$, the vibrational relaxation times $p\tau$, and the corresponding rate constants k are reported. In Fig. 1 some of the molecular absorption curves measured for CF_3Cl are presented for illustration. The absorption curve at 163 K is not complete due to the restriction caused by the vapor pressure of the substance. The relaxing vibrational energy would be still high enough to extend the measurements to lower temperatures. This range is accessible, if experiments are performed with a frequency which is much smaller than the frequency of 50 kHz employed in the present experiments. The influence of the classical absorption is small and was neglected (see Figure 1).

Table 1. Experimental results for CF_3Cl, CF_3Br, CHF_2Cl, and CH_3Cl.

Compound	T [K]	$(\nu/p)_{\max}$ [MHz/bar]	$p\tau$[a] [µs bar]	k[b] [$cm^3\,s^{-1}$]
CF_3Cl	294	1.3	0.26	$1.5 \cdot 10^{-13}$
	271	1.2	0.27	$1.4 \cdot 10^{-13}$
	243	1.1	0.27	$1.2 \cdot 10^{-13}$
	223	1.0	0.29	$1.1 \cdot 10^{-13}$
	203	0.95	0.29	$0.97 \cdot 10^{-13}$
	188	0.90	0.29	$0.89 \cdot 10^{-13}$
	178	0.92	0.27	$0.90 \cdot 10^{-13}$
	168	0.95	0.25	$0.91 \cdot 10^{-13}$
	163	1.0	0.24	$0.95 \cdot 10^{-13}$
CF_3Br	296	1.9	0.19	$2.1 \cdot 10^{-13}$
	273	1.7	0.20	$1.9 \cdot 10^{-13}$
	244	1.6	0.20	$1.7 \cdot 10^{-13}$
	223	1.6	0.19	$1.6 \cdot 10^{-13}$
	198	1.6	0.18	$1.5 \cdot 10^{-13}$
	193	1.6	0.17	$1.5 \cdot 10^{-13}$
CHF_2Cl	295	3.5	0.084	$4.8 \cdot 10^{-13}$
	271	3.6	0.078	$4.8 \cdot 10^{-13}$
	248	4.2	0.063	$5.4 \cdot 10^{-13}$
	228	4.9	0.051	$6.1 \cdot 10^{-13}$
	213	5.1	0.047	$6.2 \cdot 10^{-13}$
	198	5.6	0.041	$6.5 \cdot 10^{-13}$
CH_3Cl	296	1.05	0.19	$2.1 \cdot 10^{-13}$
	273	1.1	0.17	$2.1 \cdot 10^{-13}$
	243	1.2	0.15	$2.2 \cdot 10^{-13}$
	233	1.2	0.15	$2.1 \cdot 10^{-13}$
	223	1.3	0.14	$2.2 \cdot 10^{-13}$

[a] $p\tau = [2\pi(\nu/p)_{\max}]^{-1} (C_p^0 C_v^0 / C_p^\infty C_v^\infty)^{1/2}$.
[b] $k = RT/N_L p\tau$.

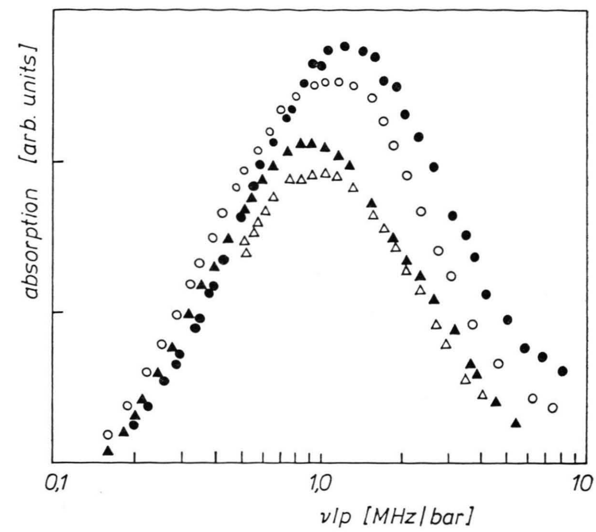

Fig. 1. Ultrasonic absorption curves measured at different temperatures for CF_3Cl: ● $T = 294$ K, ○ $T = 223$ K, ▲ $T = 178$ K, and △ $T = 163$ K.

For a gneral discussion of the temperature dependence of $V-R, T$ rate constants k we define an energy parameter which may vary with temperature:

$$-\,d \ln k / d(1/RT) = E\,. \tag{1}$$

A statistical interpretation analogous to that given in [12a–12c] for chemical reactions yields:

$$E = \langle E_{\mathrm{in,th}} \rangle - \langle E_{\mathrm{th}} \rangle\,, \tag{2}$$

where $\langle E_{\mathrm{in,th}} \rangle$ is the average thermal energy of molecule pairs performing inelastic collisions and $\langle E_{\mathrm{th}} \rangle$ is the average thermal energy of all colliding molecule pairs.

According to (1) the experimental results are discussed by plotting $\log(k)$ versus $1/T$. Figure 2 shows such a plot for CF_3Cl and CF_3Br including also high temperature data from [7]. There is a good agreement between these high temperature data and the present low temperature results. For comparison, the corresponding CF_4-data [8] are also presented in Figure 2. In an analogous presentation our results for CHF_2Cl and CH_3Cl together

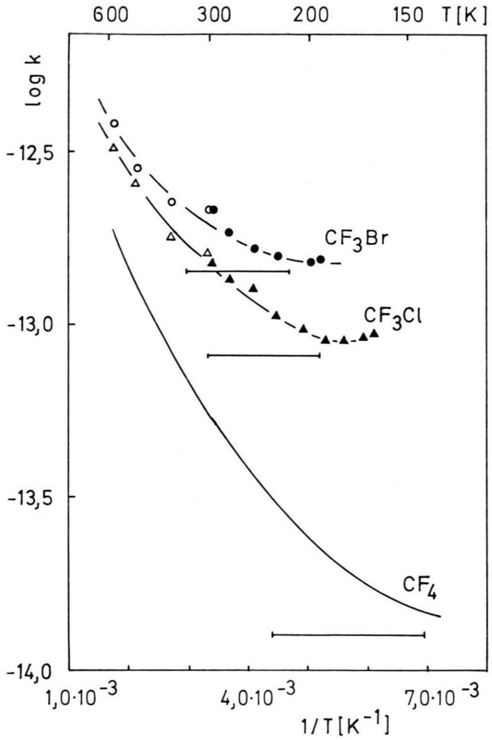

Fig. 2. Plot of log k versus $1/T$; CF_3Cl: ▲ present results, △ Ref. [7]; CF_3Br: ● present results, ○ Ref. [7]; CF_4: Ref. [8] and references given therein. The horizontal bars indicate the reference interval $T_{crit} - T_{boil}$; CF_3Cl: 302 — 192 K; CF_3Br: 340 — 214 K; CF_4: 227 — 144 K.

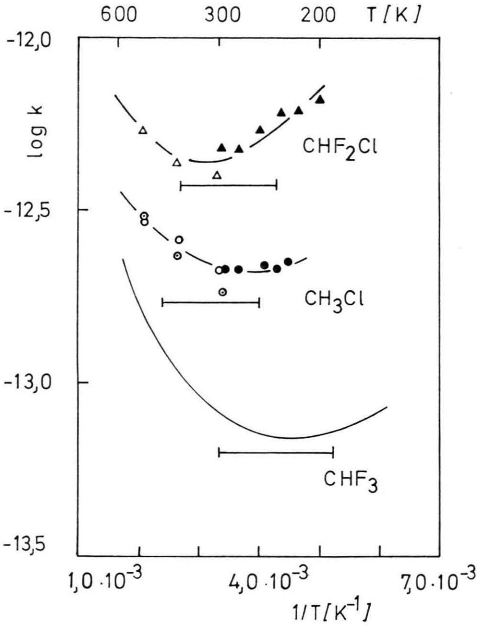

Fig. 3. Plot of log k versus $1/T$; CHF_2Cl: ▲ present results, △ Ref. [7]; CH_3Cl: ● present results, ○ Ref. [7], ⊙ Ref. [9]; CHF_3, Ref. [8]. The horizontal bars indicate the reference interval $T_{crit} - T_{boil}$; CHF_2Cl: 369 — 232 K; CH_3Cl: 417 — 249; CHF_3: 299 — 191 K.

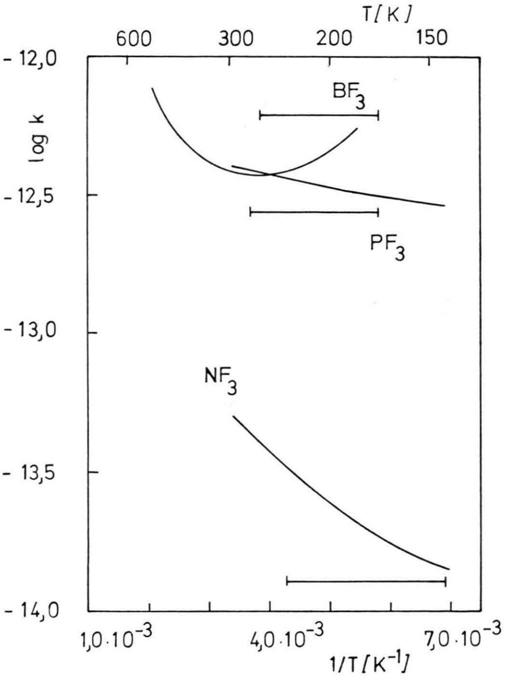

Fig. 4. Plot of log k versus $1/T$: BF_3 Ref. [10], NF_3 Ref. [11] and PF_3 Ref. [11]. The horizontal bars indicate the reference interval $T_{crit} - T_{boil}$; BF_3: 261 — 173 K; NF_3: 234 — 144 K; PF_3: 271 — 172 K.

with high temperature data available from the literature are shown in Figure 3. For CH_3Cl the data reported in [7] are in good agreement with the present room temperature results, whereas in the case of CHF_2Cl the room temperature data from [7] and the present results do not agree. In addition, Fig. 3 gives the relaxation behavior of CHF_3 for completeness [8]. In Fig. 4, earlier results are collected for the three fluorides NF_3, PF_3, and BF_3, which show different types of low temperature behavior [10], [11].

Discussion

As can be seen from Figs. 2—4, the slope of a plot of log(k) versus $1/T$ can be positive, negative or zero. The behavior depends on the value of the right hand side of (1). Accordingly, we will classify inelastic collisions as follows:

Class I: $\langle E_{in,th} \rangle > \langle E_{th} \rangle$. The average thermal energy of molecule pairs performing inelastic collisions is larger than the average thermal energy of all collision pairs. This behavior is observed for $V-R, T$ transfer at temperatures above the critical temperature. In this region the simple Landau-Teller or SSH model may be applied and the resulting $T^{-1/3}$-temperature dependence is confirmed within experimental error in many systems. According to this model inelastic processes are mainly due to collisions occurring with a much higher translational energy than the average value calculated from the Maxwell-Boltzmann distribution [4]. With increasing temperature the number of these high energy collisions increases drastically and, therefore, energy transfer becomes more effective at higher temperatures.

Class II: $\langle E_{\text{in, th}} \rangle \approx \langle E_{\text{th}} \rangle$. In this case, the average thermal energy of collisions producing transitions between vibrational states is similar to the average thermal energy of all colliding molecule pairs. This behavior can be expected at low temperatures, when the collisions dynamics is determined mainly by the attractive forces acting at small distances between the colliding molecules. The influence of the thermal motion on energy transfer dies out with decreasing temperature and, therefore, a constant value of the rate constant may be approached.

Class III: $\langle E_{\text{in, th}} \rangle < \langle E_{\text{th}} \rangle$. The average energy of all colliding molecule pairs is larger than that of the collision pairs producing vibrational transitions. This means that thermal motion obviously disturbs the energy exchange process. The resulting inverse temperature dependence may be explained by the fact that with decreasing temperature the disorganizing effect of thermal motion is more and more overcome by the influence of the intermolecular potential. This low temperature interaction leads to enhanced energy transfer.

Detailed collision models, which try to understand the dynamics of those collisions, reach from orientational effects due to the anisotropy of the interaction potential [1] to transient interacting pairs or complex formation [14], [19].

Using this classification as a guide, the low temperature data presented in Figs. 2—4 will be discussed in more detail now.

Class II behavior is characterized by an approximately constant value of the rate constant over a large temperature range. The superposition of class I and class III behavior, of course, may also lead to a nearly constant value, but only in a small temperature region. To compare the relaxation behavior of different molecules, a reference temperature interval must be selected. It seems to be reasonable to use the critical point to boiling point region, because these well known macroscopic properties correlate with the intermolecular well depth, at least for isotropic molecules [13]. This means that not only thermal motion, but also intermolecular attraction plays an important role in this temperature region. In the reference interval $T_{\text{crit}} - T_{\text{boil}}$, which is indicated by a horizontal bar in Figs. 2—4, the rate constant for $V-R, T$ transfer in the symmetric CF_4 molecule is strongly decreasing (class I behavior). A reduction of the symmetry by substitution of one F-atom by a Cl- or Br-atom yields a nearly constant value of the rate constant already around the boiling point. For CF_3Cl the results indicate a possible inverse temperature dependence at somewhat lower temperatures (see Figure 2). Thus, we may conclude that in less symmetric, more polar molecules, class II and class III behavior moves toward higher temperatures. This conclusion is confirmed by the data given in Fig. 4 for the molecules NF_3, PF_3, and BF_3. From NF_3 to PF_3, the polarity of the pyramidal structure is increased and, in fact, the slope is much smaller for PF_3 than for NF_3 in the reference interval. The drastic change of the relaxation behavior going to BF_3, is connected with the transition from a pyramidal to a planar structure with a vanishing dipole moment. This comparison indicates that polarity plays an important role, however no simple correlation exists between dipole moment and class II and class III behavior. It is interesting to compare the behavior of CH_3Cl ($\mu = 1.87$ D) and CHF_2Cl ($\mu = 1.42$ D) in this respect. Within experimental error, CH_3Cl shows class I and class II behavior between critical temperature and boiling point, whereas CHF_2Cl possesses an inverse temperature dependence near the boiling point. Comparing the behavior of $V-R, T$ rates with the symmetry and dipole moment of the investigated molecules, we find some correlation. Such a correlation seems to be less stringent for the dipole moment which measures the polarity at long distances.

The statistical interpretation leads to the result that in the case of class III behavior the mean thermal energy of inelastically colliding pairs is smaller than that of all colliding pairs. This condition seems to be reasonable for collisions leading to transient interacting pairs or complexes. Such a mechanism is discussed in detail in [14] for state changes induced predominately by attractive forces. For processes with cross sections approaching or exceeding hard sphere values, a correlation between an effective intermolecular well depth ε', and the inelastic cross section q is discussed in [14]:

$$\ln q = \ln C + \varepsilon'/kT\,, \tag{3}$$

where C is a constant. For near resonant vibration to vibration transfer, this condition seems to be fulfilled in many cases, and an effective well depth 1.6 times larger than the Lennard-Jones well depth ε is determined from $V-V$ transfer data of hydrogen halides [15]. In $V-R, T$ processes, normally, a much larger energy gap is involved than for $V-V$ transfer, leading to much smaller cross sections. Despite this fact, a correlation of low temperature $V-R, T$ data seems to be possible in some cases as shown in [16]. Correlating transition probabilities gives a different effective well depth than, for example, correlation of cross sections or rate constants. Correlating cross sections as in [14] and [15], we find for CHF_2Cl an effective well depth of 390 K, which is about 1.6 times larger than the Lennard-Jones value reported in [17]. For CHF_3 the effective well depth found in this way, however, is comparable to the Lennard-Jones well depth. In the case of BF_3 the effective well depth obtained is 460 K. This is about 2.6 times the Lennard-Jones well depth of 178 K given in [18]. This result correlates with anomalous values of thermodynamic properties such as enthalpy and entropy of vaporization, indicating a strong interaction between BF_3 molecules [10]. We wish to point out that the values given above for the effective well depths are not very accurate. They are determined from the inverse temperature dependence which has been investigated so far only in the relatively small temperature intervals of 200—270 K for CHF_2Cl, 160—210 K for CHF_3, and 180—240 K for BF_3.

For molecules with an anisotropic interaction potential, the well depth for an orientation favourable for energy transfer may be much larger than the averaged Lennard-Jones well depth. In [1] an energy transfer mechanism is discussed which is based on oriented collisions induced by an anisotropic dipole-dipole interaction. This model can explain class III behavior of CHF_3 and CHF_2Cl, however, one should keep in mind, that for inelastic collisions short-distance interaction is important. Adopting the concept of oriented collisions, BF_3 would be an example that clearly shows that the kind of anisotropic interaction which may be important for energy transfer is not confined to dipole interaction. The situation becomes quite complex when the orientation most favourable for interaction and the orientation most favourable for energy exchange do not coincide.

Conclusions

To compare the different low temperature behavior of energy transfer rate constants of the molecules CF_4, CF_3Cl, CF_3Br, CF_3H, CHF_2Cl, CH_3Cl, NF_3, PF_3, and BF_3, the temperature interval $T_{\text{crit}} - T_{\text{boil}}$ is selected as reference. The statistical point of view adopted for inelastic collisions allows a general discussion of relaxation behavior. These statistical considerations show that thermal motion and intermolecular collision dynamics may work together to induce energy exchange or may counteract. At high temperatures energy transfer is enhanced by additional thermal energy and the essential features of the exchange process can be described by relatively simple models (class I behavior). All systems approach more ore less slowly a constant value of the rate constant below the critical temperature. Such a behavior may be expected, for example, if all collision pairs possess the same energy due to the increasing influence of attractive forces. Then, the collision pairs performing inelastic collisions possess a similar energy as all collision pairs and the rate constant no longer depends on temperature (class II behavior). The rate constants of several molecules (e.g. CHF_2Cl) run through a minimum in the temperature range investigated. Statistically, the effect of an inverse temperature behavior is expected, if the average energy of all colliding molecule pairs is larger than that of collision pairs producing energy exchange (class III behavior). This means thermal energy obviously hinders the performance of effective energy exchange in this temperature region.

Acknowledgements

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