Vibrational Energy Transfer in Silane and Silane Mixtures

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The vibrational relaxation time for pure SiH_4 is 0.10, 0.083 and 0.072 μsec atm (±30%) at 295 K, 375 K and 462 K. For SiH_4 diluted in He, D_2 and H_2 the corresponding numbers are 0.16, 0.081 and 0.031 μsec atm (±30%) at 295 K. The binary two-level theory has been used to determine the four V–R, T rates in the system SiH_4-CH_4, and the rate for V–V exchange between SiH_4 and CH_4 from experimental data. From the Schwartz-Slawsky-Herzfeld-formula for V–T and V–V, T processes an equation is derived describing V–R and V–V, R energy exchange. The different models are compared with experimental data, especially with those found for the system SiH_4-CH_4.

Introduction

Cottrell and Matheson compared the relaxation times of SiH_4 and SiD_4 and obtained the surprising result that SiD_4 has the longer relaxation time[1]. A model calculation of the interaction of a classical rotator and a quantized oscillator performed by these authors showed that vibrational-rotational energy transfer can account for the observed isotope effect. Thus, they concluded that in molecules with low moments of inertia like SiH_4, CH_4 etc. the interaction between the rotation of the peripheral atoms of one molecule and the vibration of another is more efficient in transferring energy than the interaction between translational motion and vibration.

The simple V-R model described the isotope effect. When the value of the repulsion parameter was selected to obtain agreement with experimental data at room temperature, the temperature dependence of the transition probability was too steep for all molecules tested[2].

A more satisfactory description of the energy transfer process could be expected from a V–R, T model, which considers rotational motion of both collision partners, as well as their relative translational motion. Such model calculations have been performed and an improved correlation of experimental data in the case of CH_4, and different CH_4 mixtures, has been found[3]. Unfortunately, an additional parameter is introduced and therefore no accurate values for the potential energy parameter can be obtained from this correlation.

The goal of this investigation was to study in more detail the mechanism of vibrational energy transfer in pure SiH_4 and in the systems SiH_4-H_2, SiH_4-D_2, SiH_4-He and SiH_4-CH_4. The temperature dependence of the transition probability in pure SiH_4 and CH_4 was compared with different model calculations. The results for the deactivation of SiH_4 by the collision partners H_2, D_2 and He were compared with the corresponding CH_4-systems, which have already been extensively studied. The most interesting rates are those obtained for the system SiH_4-CH_4 using the binary two-level theory to analyse the experimental data. These results for the different V – R, T and V – V, R, T processes have been compared with simple model calculations for V – R and V – V, R, and also for V – T and V – V, T exchanges.

Experimental

The measurements of the velocity of sound were performed in an acoustic interferometer[4]. Three quartz crystals with the frequencies 543.4 kHz, 794.2 kHz and 1.187 MHz at 295 K have been used. The frequency was determined very accurately during each measurement on a Rohde & Schwarz 100 MHz counter (type FET 2). The distance between crystal and reflector usually was changed by 10 – 20 wavelengths and could be measured with an accurate micrometer. The pressure could be varied between 5 atm and 80 torr; therefore measurements were made over the range 110 kHz/atm – 11 MHz/atm. To correct for gas imperfections, the second virial coefficient for pure SiH_4 was determined from viscosity data and for its mixtures using the method described in Reference[5]. The following Messer-Griesheim research-grade gases were used without further purification: SiH_4 99.9%; CH_4 99.999%; H_2 99.999%; D_2 99.7% and He 99.996%.

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Results

1. SiH_4

For pure SiH_4, measurements were made at the temperatures $T = 295$ K, $T = 375$ K and $T = 462$ K. The results obtained are shown in Table I together with the values reported by Cottrell and Matheson [1]. The differences are small compared with the experimental error. In SiH_4 the asymmetric bending mode ($\nu_4 = 913.3$ cm^{-1}) and the symmetric bending mode ($\nu_2 = 972.1$ cm^{-1}) have similar frequencies which are much lower than those of the stretching modes ($\nu_1 = 2185.7$ cm^{-1} and $\nu_3 = 2189.1$ cm^{-1}) [6]. Thus, at lower temperatures the vibrational energy is concentrated mainly in the bending modes and we can calculate a transition probability for the deactivation of the bending modes [7]:

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

System	Temperature [K]	$p\tau$ [μsec atm]	$P = (\tau Z)^{-1}$	P_{10} [Eq. (2)]
SiH_4	295	0.10 ±0.03	$1.3 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$
SiH_4	298 [1]	0.11 ±0.06	$1.2 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$
SiH_4	348 [1]	0.10 ±0.06	$1.4 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$
SiH_4	375	0,083 ±0.03	$1.7 \cdot 10^{-3}$	$2.8 \cdot 10^{-3}$
SiH_4	462	0,072 ±0.03	$2.2 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$
SiH_4-H_2	295	0.031 ±0.01	$1.9 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$
SiH_4-D_2	295	0.081 ±0.03	$1.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$
SiH_4-He	295	0,16 ±0.05	$5.6 \cdot 10^{-4}$	$8.7 \cdot 10^{-4}$

$$P = (\tau Z)^{-1} . \tag{1}$$

The values given in Table I are obtained by using the hard sphere expression to determine the collision frequency Z and a collision diameter of $\sigma = 4.0$ Å for SiH_4.

Usually investigators calculate a transition probability P_{10} for the deactivation of the lowest mode, assuming that the vibrational modes are in rapid equilibrium and that energy transfer goes through the lowest mode [7]:

$$P_{10} = \{(C_{\nu_{\min}} / \sum_i C_{\nu_i}) \, \tau Z [1 - \exp\{-h \nu_{\min}/k T\}]\}^{-1} . \tag{2}$$

These values are shown in Table I also.

2. SiH_4-H_2, SiH_4-D_2 and SiH_4-He

The vibrational relaxation times in the mixtures SiH_4-H_2, SiH_4-D_2 and SiH_4-He have been determined at $T = 295$ K for three different mole fractions, Figure 1. The plots show the expected linear behavior of the reciprocal relaxation time versus mole fraction. The relaxation times, determined from these measurements for the deactivation of SiH_4 by the collision partners H_2, D_2 and He, are indicated in Table I. In addition, as described before, the transition probabilities P and P_{10} have been calculated using the collision diameters for H_2, D_2 and He given in Reference [5]. From Table I we see that D_2 is more effective than He, which have the same mass; and that H_2 is the most effective collision partner. Qualitatively, this is the same behavior as found for the corresponding CH_4-mixtures [8, 9]. The transition probabilities are substantially higher in SiH_4-mixtures due to the lower frequencies of the bending vibrations in SiH_4. The similarity between SiH_4 and CH_4 suggests a similar mechanism of energy transfer in both molecules. Therefore, we may guess as suggested for the corresponding CH_4 mixtures that rotation in H_2 and D_2 causes the high efficiency of these collision partners; but we do not know exactly at this time how rotation is involved in the energy transfer processes.

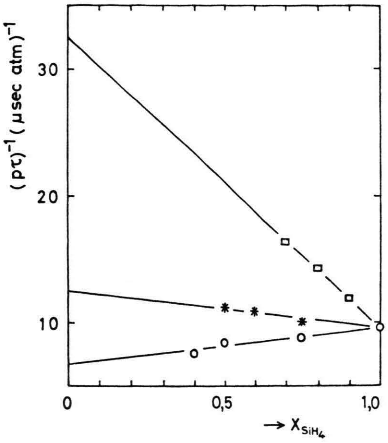

Fig. 1. $1/p\tau$ versus mole fraction for the deactivation of SiH_4 by different collision partners: ○ SiH_4-He; * SiH_4-D_2 and □ SiH_4-H_2.

3. SiH_4-CH_4

The results obtained at $T = 295$ K for different mole fractions in the system SiH_4-CH_4 are shown in Figure 2. In each mixture a single dispersion step was observed from which one relaxation time

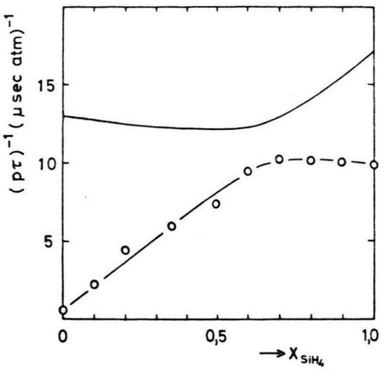

Fig. 2. $1/p\,\tau$ versus mole fraction for the system SiH_4-CH_4: ○ experimental results, ——— calculated conic section using the $p\,\tau$ values from Table II.

could be calculated. The dispersion widths found experimentally were in good agreement with those calculated using the whole vibrational heat capacity of the corresponding mixtures. In CH_4 the $V-V$ rates are fast compared to the $V-R, T$ rate[10, 11], and the same may be expected for SiH_4 however, the difference in the rates will be smaller. If we assume that all contributions to the vibrational heat capacity relax in these molecules with comparable rates determined by the de-excitation probability of the lowest level, we can describe SiH_4 and CH_4 approximately as two-level gases, Figure 3.

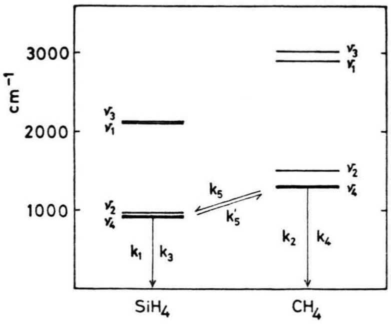

Fig. 3. Energy level diagram for SiH_4 and CH_4 showing the five rates determined by the binary two-level theory.

For a binary two-level gas mixture a theory is available to determine the five rate constants shown in Figure 3[12]. According to this theory, the isothermal relaxation rate $1/\tau^0_{VRT}$ of a mixture is given by the expression

$$\left(\frac{1}{\tau^0_{VRT}}-\frac{x_A}{\tau^0_{AA}}-\frac{x_B}{\tau^0_{AB}}\right)\cdot\left(\frac{1}{\tau^0_{VRT}}-\frac{x_A}{\tau^0_{BA}}-\frac{x_B}{\tau^0_{BB}}\right) \qquad (3)$$
$$-x_A\,x_B\,k_5\,k_5'=0\,.$$

This is an equation for a conic section going through the points $1/\tau^0_{AA}$, $1/\tau^0_{BA}$ at $x_A=1$ and $1/\tau^0_{BB}$, $1/\tau^0_{AB}$ at $x_B=1$.

The values for these four points of intersection are obtained from the measured curve. With the relationships

$$\begin{aligned}
1/\tau^0_{AA}&=\left(1+\frac{\bar{C}_{A_1}}{\bar{C}_{A_0}}\right)k_1\,;\\
1/\tau^0_{BA}&=\left(1+\frac{\bar{C}_{B_1}}{\bar{C}_{B_0}}\right)\left(k_3+\frac{k_5'}{1+\bar{C}_{A_1}/\bar{C}_{A_0}}\right);\\
1/\tau^0_{BB}&=\left(1+\frac{\bar{C}_{B_1}}{\bar{C}_{B_0}}\right)k_4\,;\\
1/\tau^0_{AB}&=\left(1+\frac{\bar{C}_{A_1}}{\bar{C}_{A_0}}\right)\left(k_2+\frac{k_5}{1+\bar{C}_{B_1}/\bar{C}_{B_0}}\right),
\end{aligned} \qquad (4)$$

and a fifth point, the five rate constants can be derived. Thus, the analysis of the experimental results with the binary two-level theory yields the relaxation times for $V-V$ exchange if the ratio k_5/k_5' is known, and also yields the four $V-R, T$ rates, namely, deactivation of SiH_4 by SiH_4 and CH_4 and deactivation of CH_4 by CH_4 and SiH_4. Only one branch of the conic section has been observed experimentally. Larger deviations of the

Table II. Relaxation times for the system SiH_4-CH_4 and comparison between experimental and theoretical transition probabilities.

Process	Type	$p\,\tau$ [μsec atm]	P^{01}_{10}(V−V, R, T) resp. P_{10}(V−R, T) experimental	P_{10}(V−R) eq. (4) ref. [2]	P^{01}_{10}(V−V, T) resp. P_{10}(V−T) eq. (5)	P^{01}_{10}(V−V, R) resp. P_{10}((V−R) eq. (6)
$SiH_4^*+CH_4=CH_4^*+SiH_4$	V−V, R, T	0.92 ± 0.5	$1.2\cdot10^{-4}$		$5.1\cdot10^{-4}$	$1.4\cdot10^{-3}$
$CH_4^*+SiH_4=SiH_4^*+CH_4$	V−V, R, T	0.14 ± 0.07	$7.9\cdot10^{-4}$		$3.5\cdot10^{-3}$	$9.4\cdot10^{-3}$
$SiH_4^*+SiH_4=2\,SiH_4$	V−R, T	0.10 ± 0.03	$2.0\cdot10^{-3}$	$2.1\cdot10^{-3}$	$5.7\cdot10^{-5}$	$1.4\cdot10^{-2}$
$SiH_4^*+CH_4=SiH_4+CH_4$	V−R, T	0.084 ± 0.03	$2.1\cdot10^{-3}$	$2.1\cdot10^{-3}$	$3.1\cdot10^{-4}$	$1.2\cdot10^{-2}$
$CH_4^*+CH_4=2\,CH_4$	V−R, T	1.6 ± 0.4	$8.3\cdot10^{-5}$	$8.3\cdot10^{-5}$	$2.5\cdot10^{-5}$	$1.1\cdot10^{-3}$
$CH_4^*+SiH_4=CH_4+SiH_4$	V−R, T	$0.10\pm^{0.2}_{0.03}$	$1.4\cdot10^{-3}$	$8.3\cdot10^{-5}$	$6.0\cdot10^{-6}$	$1.3\cdot10^{-3}$

conic section from the measured curve could therefore occur in the mole fraction region 0.3 – 0.7 [13]. To test the accuracy of the data analysis the relaxation times derived from the experimental curve (see Table II) have been used to calculate the corresponding conic section with Equation (3). From Fig. 2 we see that the experimental curve is in close agreement with the corresponding branch of the calculated conic section. Nevertheless, the relaxation times derived must be considered with caution because a two-level theory has been applied to polyatomic molecules in which more than two levels are excited appreciably and only one branch of the conic section could be observed. The most inaccurate rates are the V – V rates and the V – R, T rate for the deactivation of CH_4 by SiH_4. The latter rate is strongly influenced by the corresponding V – V rate which has a similar magnitude [see appropriate Equation (4)]. Therefore, it is necessary to compare these relaxation times with values measured by another method to determine the accuracy of the two-level-approximation used; but no such values are available at this time.

The transition probabilities P_{10}^{01} and P_{10} shown in Table II have been calculated from the corresponding relaxation times in column three using Eq. (1) for the V – V, R, T and Eq. (2) for the V – R, T probabilities and $\sigma = 3.8$ Å as collision diameter for CH_4.

Discussion

In the following section we derive a V – R model in which rotation is treated on the same level as translation in the SSH-theory. To compare the simple V – R and V – T models and to calculate the rates for V – V exchange in the system $SiH_4 - CH_4$ we used the theory derived by Schwartz, Slawsky and Herzfeld [14], and extended by Tanczos [15], Stretton [16] and Yardley, Moore [10]:

$$P_{k-l}^{i-j}(a,b) = P_0(a)\,P_0(b)\,g_j\,g_l\,V_{i-j}^2(a)\,V_{k-l}^2(b)\,J(\varDelta E, T, L, \mu, \varepsilon)\,, \tag{5}$$

$$J = \frac{256\,\pi^6 L^4 \mu^3 \varDelta E^2}{h^4\,k\,T} \exp\left\{\frac{\varepsilon}{k\,T}\right\} \int\limits_0^\infty \frac{\exp\{4\,\pi^2 L\,\mu\,v\,[1-(1+2\,\varDelta E/\mu\,v^2)^{1/2}]\,h^{-1}\}}{(1-\exp\{4\,\pi^2 L\,\mu\,v\,[1-(1+2\,\varDelta E/\mu\,v^2)^{1/2}]\,h^{-1}\})^2} \exp\left\{-\frac{\mu\,v^2}{2\,k\,T}\right\} v\,\mathrm{d}v$$

where $P_0(a)$ and $P_0(b)$ are steric factors, g_j and g_l the degeneracy of state j and l, $V_{i-j}^2(a)$ and $V_{k-l}^2(b)$ the vibrational matrix elements; the integral J has been determined numerically. Equation (5) can be used to calculate transition probabilities for V – T and V – V, T processes.

A similar theory for V – R and V – V, R processses may be derived by substituting "$\omega\,d$" for the translational relative velocity and "I/d^2" for the reduced mass where ω is the angular frequency of the rotator, d the distance from the axis of rotation to the rotating peripheral atom and I the moment of inertia of the rotator:

$$P_{k-l}^{i-j}(a,b) = P_0(a)\,P_0(b)\,g_j\,g_l\,V_{i-j}^2(a)\,V_{k-l}^2(b)\,J(\varDelta E, T, L, I/d^2, \varepsilon)\,, \tag{6}$$

$$J = \frac{256\,\pi^6 L^4 I^3 \varDelta E^2}{h^4\,d^6\,k\,T} \exp\left\{\frac{\varepsilon}{k\,T}\right\} \int\limits_0^\infty \frac{\exp\{4\,\pi^2 L\,\omega\,I/d\,[1-(1+2\,\varDelta E/I\,\omega^2)^{1/2}]\,h^{-1}\}}{(1-\exp\{4\,\pi^2 L\,\omega\,I/d\,[1-(1+2\,\varDelta E/I\,\omega^2)^{1/2}]\,h^{-1}\})^2} \exp\left\{-\frac{I\,\omega^2}{2\,k\,T}\right\} \omega\,\mathrm{d}\omega\,.$$

Using Eq. (5) and (6) a reasonable comparison between V – R and V – T models and also between V – V, R and V – V, T models seems possible. The main problem is to determine the value of the potential energy parameter. For CH_4 elastic scattering data yield $L = 0.25$ Å [22] but for SiH_4 no experimental data are available. The procedure of fitting an exponential to a Lennard-Jones potential, as proposed by Herzfeld, gives values between 0.18 and 0.22 Å for CH_4 and 0.19 and 0.23 Å for SiH_4 [23]. Herzfeld's procedure, which has been fairly successful for a large number of simple molecules, gives values around $L = 0.2$ Å for the repulsion parameter; therefore, we selected $L = 0.2$ Å for SiH_4 and CH_4. The steric factor is another parameter in these theories and the usual value $P_0 = 1/3$ has been chosen unless otherwise stated. The vibrational matrix elements for CH_4 and SiH_4 were estimated according to Ref. [10] using $(\overline{A}^2)_{CH_4} = 0.209$ amu^{-1} and $(\overline{A}^2)_{SiH_4} = 0.24$ amu^{-1}.

The V – T results obtained from Eq. (5) are plotted in Fig. 4 and Fig. 5 as dashed lines for SiH_4

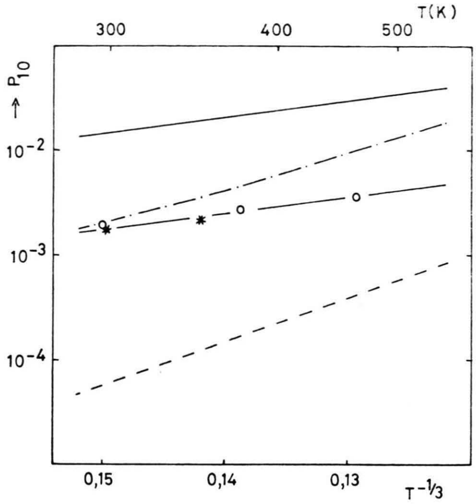

Fig. 4. Transition probability versus $T^{-1/3}$ for pure SiH_4: ○ this work; * Ref.[1]; ——— V–R model Eq. (6) upper line $P_0=1/3$, line through experimental points $P_0=0{,}04$; – – – V–T model Eq. (5); — · — · — V–R model Eq. (4) Ref.[2].

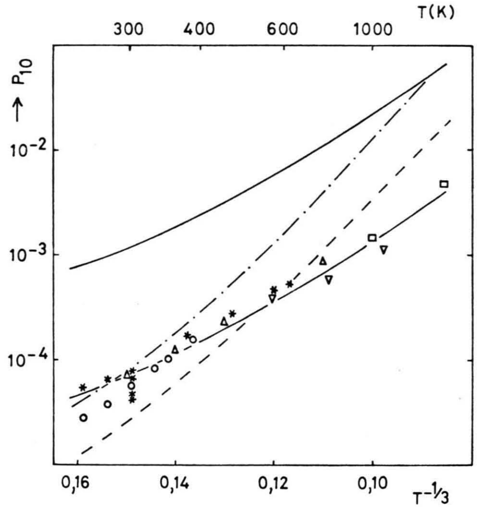

Fig. 5. Transition probability versus $T^{-1/3}$ for pure CH_4: * results collected in Ref.[17]; ○ Ref.[18]; □ Ref.[19]; ▽ Ref.[20]; △ Ref.[21]; ——— V–R model Eq. (6) upper line $P_0=1/3$, line through experimental points $P_0=0{,}02$; – – – V–T model Eq. (5), — · — · — V–R model Eq. (4), Ref.[2].

and CH_4 respectively. The temperature dependence is too steep as already found for CH_4 by other authors. In addition the absolute transition probabilities are very low in the case of SiH_4 compared to the experimental values. Smaller values of the repulsion parameter would be necessary, to describe the temperature dependence; but as discussed before, the value chosen is already lower than scattering data indicate. The transition probabilities for the four $V-T$ processes in the system SiH_4-CH_4 at 295 K appear in column six of Table II. In addition, the probabilities for $V-V, T$ exchange processes are shown in this column. These latter values are in much closer agreement with the experimental results than the $V-T$ rates which do not describe the data adequately.

Better results should be expected from the $V-R$ model using Eq. (6), because SiH_4 and CH_4 have relatively small moments of inertia. The upper solid lines in Fig. 4 and Fig. 5 belong to a steric factor $P_0=1/3$ and lower lines drawn through the experimental points were calculated using the rather small steric factors $P_0=0.04$ for pure SiH_4 and $P_0=0.02$ for pure CH_4. These plots show clearly that the temperature dependence is described within experimental error for SiH_4 and CH_4, but the absolute values of the transition probabilities are too high. The probabilities for the different $V-R$ and $V-V, R$ processes in the system SiH_4-CH_4 at 295 K are collected in column seven of Table II. The results for three $V-R$ and the $V-V, R$ processes are about one order of magnitude too high. Agreement is obtained only for the deactivation of CH_4 by SiH_4, but this may be fortuitous. If, for example, a correction factor is introduced due to vibrational anharmonicities, as found for $V-T$ transfer, the transition probabilities reduce by a factor of 10^{-1} to 10^{-2}[24]. Then only for the deactivation of CH_4 by SiH_4 would larger discrepancies appear if we assume a similar anharmonic correction factor for the $V-R$ model.

For comparison in Fig. 4 and Fig. 5 the curves are shown as intermittent lines which have been calculated using Eq. (4) of Ref.[2] and $P_0=1/5$ and $L=0.34$ Å as proposed in this paper. The temperature dependence for pure SiH_4 and CH_4 is too steep, and the theoretical curves intersect the experimental curves near room temperature. The transition probabilities for the $V-R$ processes in the system SiH_4-CH_4 at 295 K are in close agreement with experimental data; only the value for the deactivation of CH_4 by SiH_4 is too small. Clearly the values of the parameters P_0 and L have been selected in this case to fit the room temperature data, but nevertheless it is surprising that although the deactivation of SiH_4 by CH_4 is described by the theory significantly great deviations appear for the deactivation of CH_4 by SiH_4. As already mentioned the experimental rate for this latter process must be considered with caution; we are not sure whether these deviations are due to an inadequate energy transfer model, the analysis of the experimental data with the binary two-level theory, or both. If we use our values $P_0 = 1/3$ and $L = 0.2$ Å in Eq. (4) of Ref. [2], we also find a slope comparable with the experimental one; but the probabilities are two orders of magnitude too high in the case of pure SiH_4, and even more for CH_4. Therefore, we may conclude that Eq. (6) is in somewhat better agreement with experimental results than Eq. (4) of Reference [2].

Conclusion

The main problem in the comparison of different energy transfer models is our ignorance concerning the intermolecular potential. The best we can hope for at this time are order of magnitude calculations. If we take the value $L = 0.2$ Å for the repulsion parameter in SiH_4 and CH_4 as suggested by transport properties, the $V-R$ model [Eq. (6)] describes the measured temperature dependence of the transition probability in pure SiH_4 and CH_4. The $V-T$ model would describe the measured slope only with considerably smaller L-values and this seems unlikely because elastic scattering data yield values $L > 0.2$ Å.

The collision partners H_2, D_2 and He show the same behavior concerning the deactivation of SiH_4 as already observed for the corresponding CH_4 systems. Thus, we conclude that a similar mechanism of vibrational energy transfer occurs in the SiH_4- and CH_4-systems.

To analyse the acoustic measurements obtained for the $SiH_4 - CH_4$ mixtures, the binary two-level theory has been used; the four $V-R, T$ rates and the rates for $V-V, R, T$ exchange processes are determined. The accuracy of the two-level approximation should be tested by comparison with directly measured values for the $V-V, R, T$ exchange and the heterogeneous deactivation processes. The $V-V, T$ and $V-V, R$ models yield similar transition probabilities for the system $SiH_4 - CH_4$ and this implies that both processes contribute to the energy exchange. For the value of the repulsion parameter $L = 0.2$ Å used here, the $V-V, R$ model gives transition probabilities in somewhat better agreement with the experimental data than the $V-V, T$ model. For the $V-R, T$ processes in the system $SiH_4 - CH_4$, the $V-T$ model gives transition probabilities which are too low. Smaller L-values are necessary to remove these discrepancies and to describe the temperature dependence as discussed before. On the other hand the $V-R$ model yields too high transition probabilities for three $V-R, T$ processes, but does yield the correct temperature dependence. The deviations are within the error limit for such model calculations; and if an L-value around 0.2 Å should be confirmed by inelastic scattering data, it would be worth while to refine the simple $V-R$ model to take into account the anharmonicity correction [24] and the light atom effect [25]. Correct values for the transition probabilities can only be expected after these effects are taken into consideration. These correction factors do not effect the temperature dependence appreciably.

Acknowledgements

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