Vibrational Energy Transfer in Silane and Silane Mixtures

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The vibrational relaxation time for pure SiH₄ is 0.10, 0.083 and 0.072 μsec atm (± 30%) at 295 K, 375 K and 462 K. For SiH₄ diluted in He, D₂ and H₂, the corresponding numbers are 0.16, 0.081 and 0.031 usec atm (± 30%) at 295 K. The binary two-level theory has been used to determine the four V—R, T rates in the system SiH₄—CH₄, and the rate for V—V exchange between SiH₄ and CH₄ 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 SiH₄—CH₄.

Introduction

Cottrell and Matheson compared the relaxation times of SiH₄ and SiD₄ and obtained the surprising result that SiD₄ has the longer relaxation time. 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 SiH₄, CH₄ 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.

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 CH₄ and different CH₄ mixtures, has been found. 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 SiH₄ and in the systems SiH₄—H₂, SiH₄—D₂, SiH₄—He and SiH₄—CH₄. The temperature dependence of the transition probability in pure SiH₄ and CH₄ was compared with different model calculations. The results for the deactivation of SiH₄ by the collision partners H₂, D₂ and He were compared with the corresponding CH₄-systems, which have already been extensively studied. The most interesting rates are those obtained for the system SiH₄—CH₄ 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. 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 FET2). 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 SiH₄ 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: SiH₄ 99.9%; CH₄ 99.999%; H₂ 99.999%; D₂ 99.7% and He 99.996%.
Results

1. SiH₄

For pure SiH₄, measurements were made at the temperatures \(T = 295\,\text{K}, \, T = 375\,\text{K}\) and \(T = 462\,\text{K}\). The results obtained are shown in Table I together with the values reported by Cottrell and Matheson. The differences are small compared with the experimental error. In SiH₄ the asymmetric bending mode \(v₁ = 913.3\,\text{cm}^{-1}\) and the symmetric bending mode \(v₂ = 972.1\,\text{cm}^{-1}\) have similar frequencies which are much lower than those of the stretching modes \(v₃ = 2185.7\,\text{cm}^{-1}\) and \(v₄ = 2189.1\,\text{cm}^{-1}\). 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:

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

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 \(\sigma = 4.0\,\text{Å}\) for SiH₄.

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:

\[
P_{10} = \left\{ (C_{r_{min}}/\sum_i C_i) \tau Z [1 - \exp(-h v_{min}/kT)] \right\}^{-1}.\tag{2}
\]

These values are shown in Table I also.

2. SiH₄ – H₂, SiH₄ – D₂ and SiH₄ – He

The vibrational relaxation times in the mixtures SiH₄ – H₂, SiH₄ – D₂ and SiH₄ – He have been determined at \(T = 295\,\text{K}\) 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 SiH₄ by the collision partners H₂, D₂ 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 H₂, D₂ and He given in Reference. From Table I we see that D₂ is more effective than He, which have the same mass; and that H₂ is the most effective collision partner. Qualitatively, this is the same behavior as found for the corresponding CH₄ mixtures. The transition probabilities are substantially higher in SiH₄ mixtures due to the lower frequencies of the bending vibrations in SiH₄. The similarity between SiH₄ and CH₄ suggests a similar mechanism of energy transfer in both molecules. Therefore, we may guess as suggested for the corresponding CH₄ mixtures that rotation in H₂ and D₂ 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.

3. SiH₄ – CH₄

The results obtained at \(T = 295\,\text{K}\) for different mole fractions in the system SiH₄ – CH₄ are shown in Figure 2. In each mixture a single dispersion step was observed from which one relaxation time
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 CH₄ the V-V rates are fast compared to the V-R, T rate, and the same may be expected for SiH₄ 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

\[
\frac{1}{\tau} = \frac{x_A}{\tau_A} - \frac{x_B}{\tau_B}
\]

This is an equation for a conic section going through the points \(1/\tau_A\), \(1/\tau_B\) at \(x_A = 1\) and \(1/\tau_A\), \(1/\tau_B\) at \(x_B = 1\).

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

\[
\frac{1}{\tau_A} = \left(1 + \frac{C_{A_1}}{C_{A_0}}\right) k_1;
\]

\[
\frac{1}{\tau_B} = \left(1 + \frac{C_{B_1}}{C_{B_0}}\right) k_4;
\]

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 SiH₄ by SiH₄ and CH₄ and deactivation of CH₄ by CH₄ and SiH₄.

Only one branch of the conic section has been observed experimentally. Larger deviations of the

<table>
<thead>
<tr>
<th>Process</th>
<th>Type</th>
<th>(p \tau) [(\mu\text{sec atm})]</th>
<th>(P_{10}(V-V, R, T))</th>
<th>(P_{10}(V-R, T))</th>
<th>(P_{90}(V-V, T))</th>
<th>(P_{90}(V-R, T))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄⁺⁺CH₄ = CH₄⁺⁺SiH₄</td>
<td>V-V, R, T</td>
<td>0.92 ± 0.5</td>
<td>1.2.10⁻⁴</td>
<td>5.1.10⁻⁴</td>
<td>1.4.10⁻³</td>
<td>5.1.10⁻⁴</td>
</tr>
<tr>
<td>CH₄⁺⁺SiH₄ = SiH₄⁺⁺CH₄</td>
<td>V-V, R, T</td>
<td>0.14 ± 0.07</td>
<td>7.9.10⁻⁴</td>
<td>3.5.10⁻³</td>
<td>9.4.10⁻³</td>
<td>3.5.10⁻³</td>
</tr>
<tr>
<td>SiH₄⁺⁺SiH₄ = 2 SiH₄</td>
<td>V-R, T</td>
<td>0.10 ± 0.03</td>
<td>2.0.10⁻³</td>
<td>2.1.10⁻³</td>
<td>5.7.10⁻⁵</td>
<td>1.4.10⁻²</td>
</tr>
<tr>
<td>SiH₄⁺⁺CH₄ = SiH₄⁺⁺CH₄</td>
<td>V-R, T</td>
<td>0.084 ± 0.03</td>
<td>2.1.10⁻³</td>
<td>2.1.10⁻³</td>
<td>3.1.10⁻⁴</td>
<td>1.2.10⁻²</td>
</tr>
<tr>
<td>CH₄⁺⁺CH₄ = 2 CH₄</td>
<td>V-R, T</td>
<td>1.6 ± 0.4</td>
<td>8.3.10⁻⁵</td>
<td>8.3.10⁻⁵</td>
<td>2.5.10⁻⁵</td>
<td>1.1.10⁻⁴</td>
</tr>
<tr>
<td>CH₄⁺⁺SiH₄ = CH₄⁺⁺SiH₄</td>
<td>V-R, T</td>
<td>0.10 ± 0.2</td>
<td>1.4.10⁻³</td>
<td>8.3.10⁻⁵</td>
<td>6.0.10⁻⁶</td>
<td>1.3.10⁻³</td>
</tr>
</tbody>
</table>
conic section from the measured curve could therefore occur in the mole fraction region 0.3 – 0.7. 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 CH₄ by SiH₄. 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 $P_{ij}^0$ and $P_{ij}^1$ 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 CH₄.

**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 SiH₄ – CH₄ we used the theory derived by Schwartz, Slawsky and Herzfeld, and extended by Tanczos, Stretton and Yardley, Moore:

\[
P_{k}^j(a, b) = P_{0}^j(a) P_{0}(b) g_j g_l V_{k-j}^j(a) V_{k-l}^j(b) J(\Delta \varepsilon, T, L, \mu, \varepsilon),
\]

where $P_{0}^j(a)$ and $P_{0}(b)$ are steric factors, $g_j$ and $g_l$ the degeneracy of state $j$ and $l$, $V_{k-j}^j(a)$ and $V_{k-l}^j(b)$ 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 processes may be derived by substituting \( \omega d \) for the translational relative velocity and \( I/d^2 \) for the reduced mass where \( \omega \) 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:

\[
P_{k}^j(a, b) = P_{0}^j(a) P_{0}(b) g_j g_l V_{k-j}^j(a) V_{k-l}^j(b) J(\Delta \varepsilon, T, L, I/d^2, \omega),
\]

\[
J = \frac{256 \pi^6 L^4 \mu^3 \Delta \varepsilon^2}{h^4 k^4 T} \exp \left\{ \frac{\varepsilon}{k T} \right\} \frac{1}{(1 - \exp \left\{ \frac{4 \pi^2 L \mu v [1 - (1 + 2 \Delta \varepsilon/\mu v^2)^{1/2}] h^{-1}}{k^4} \right\})^2} \exp \left\{ -\frac{\mu v^2}{2 k T} \right\} v \, dv
\]

\[
J = \frac{256 \pi^6 L^4 \mu^3 \Delta \varepsilon^2}{h^4 d^6 k T} \exp \left\{ \frac{\varepsilon}{k T} \right\} \frac{1}{(1 - \exp \left\{ \frac{4 \pi^2 L \omega I/d [1 - (1 + 2 \Delta \varepsilon/I \omega^2)^{1/2}] h^{-1}}{k^4} \right\})^2} \exp \left\{ -\frac{I \omega^2}{2 k T} \right\} \omega \, d\omega.
\]

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 CH₄ elastic scattering data yields $L = 0.25$ Å but for SiH₄ 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 CH₄ and 0.19 and 0.23 Å for SiH₄. 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 SiH₄ and CH₄. The steric factor is another parameter in these theories and the usual value $P_{0}^j = 1/3$ has been chosen unless otherwise stated. The vibrational matrix elements for CH₄ and SiH₄ were estimated according to Ref. 10 using \( (A^2)_{\text{CH}_4} = 0.209 \) amu$^{-1}$ and \( (A^2)_{\text{SiH}_4} = 0.24 \) amu$^{-1}$.

The V – T results obtained from Eq. (5) are plotted in Fig. 4 and Fig. 5 as dashed lines for SiH₄.
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 $10^{-2}$. 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 CH₄ by SiH₄. 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 $L = 0.2 \text{ Å}$ 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 SiH₄, and even more for CH₄. 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 $L = 0.2 \text{ Å}$ for the repulsion parameter in SiH₄ and CH₄ as suggested by transport properties, the V–R model [Eq. (6)] describes the measured temperature dependence of the transition probability in pure SiH₄ and CH₄. 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 $L > 0.2 \text{ Å}$.

The collision partners H₂, D₂ and He show the same behavior concerning the deactivation of SiH₄ as already observed for the corresponding CH₄ systems. Thus, we conclude that a similar mechanism of vibrational energy transfer occurs in the SiH₄- and CH₄-systems.

To analyse the acoustic measurements obtained for the SiH₄–CH₄ 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 SiH₄–CH₄ and this implies that both processes contribute to the energy exchange. For the value of the repulsion parameter $L = 0.2 \text{ Å}$ 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 SiH₄–CH₄, 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 and the light atom effect. 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.

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