Comparison between quantum and classical mechanical reaction probabilities and rate constants for the collinear \( H + Cl_2 \) and \( D + Cl_2 \) systems is made. Different quasi-classical methods are compared and the QCRF method which fulfils the principle of detailed balance is suggested. Finally the total reaction rate constants are compared with results obtained from a simple transition state model.

1. Introduction

The by far easiest treatment of reactive scattering problems is obtained by applying classical mechanics. There has however recently been thrown some doubt upon some of the methods normally used in classical or semiclassical reactive scattering. This was done by comparing results obtained by rigorous quantum mechanical calculations and quasi-classical or semiclassical methods. So far most quantum mechanical calculations have been devoted to collinear arrangements [1–7]. Just recently coplanar and even three dimensional calculations have appeared [8–13]. The fact that only very few noncollinear calculations have been performed (mainly for the \( H + H_2 \) system) prevents an extensive study to compare classical and quantum mechanical results in more than one dimension. Thus the interest for doing collinear reactive classical trajectory calculations has increased. In ref. [7] it was found that quantum dynamical effects were very important for the \( F + H_2 \) systems and some disagreements between quantum and classical results were pointed out. Since the \( F + H_2 \) system is very quantum-like it will be of interest to see how the classical mechanical description fits more "classical" systems like \( H + Cl_2 \) and \( D + Cl_2 \). Recently some collinear quantum calculations [6] on these systems have become available. In this paper we use the LEPS potential parameters given in ref. [6] for the classical trajectory studies.

2. Quasi-classical methods

The reactions considered in this paper are

\[ A + Cl_2(v) \rightarrow ACl(v') + Cl \quad \text{forward}, \]

and the reverse
Table 1

Reaction probabilities obtained by different quasi-classical methods at 0.130 eV and 0.268 eV total energy

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Transition</th>
<th>Quasi-classical</th>
<th>Quantum mechanical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>QCF</td>
<td>QCR</td>
</tr>
<tr>
<td>0.130</td>
<td>0 \rightarrow 3</td>
<td>0.005 \pm 0.005</td>
<td>0.25 \pm 0.04</td>
</tr>
<tr>
<td>0.130</td>
<td>0 \rightarrow 4</td>
<td>0.15 \pm 0.03</td>
<td>0.23 \pm 0.04</td>
</tr>
<tr>
<td>0.268</td>
<td>0 \rightarrow 4</td>
<td>0.33 \pm 0.05</td>
<td>0.50 \pm 0.04</td>
</tr>
<tr>
<td>0.268</td>
<td>1 \rightarrow 4</td>
<td>0.26 \pm 0.04</td>
<td>0.13 \pm 0.03</td>
</tr>
<tr>
<td>0.268</td>
<td>2 \rightarrow 4</td>
<td>0.06 \pm 0.03</td>
<td>0.05 \pm 0.03</td>
</tr>
</tbody>
</table>

a) The probabilities and error limits were obtained from the equation [14]:

\[ P_{ij} = (1/N_{tot}) \left[ N_{j} / N_{i} \right]^{1/2} \]

where \( N_{tot} \) is the total number of trajectories and \( N_{j} \) the number ending in vibrational state \( j \).

\[ \text{Cl} + \text{ClA}(v') \rightarrow \text{Cl}_2(v) + \text{A} \quad \text{reverse}, \]

where A is either a H or a D atom.

The vibration is quantized initially and finally by assigning a quantum number \( v \) to values of the continuous variable in the box \( [v - \frac{1}{2}; v + \frac{1}{2}] \).

If the system is started in a given initial \( v \)-state and box quantized finally then the principle of detailed balance is not properly fulfilled. This is however, the case if also initial box quantization is used. Thus we tested the following three possibilities:

1. QCF fixed initial \( v \), final box quantization of \( v' \) (forward reaction);
2. QCR fixed initial \( v' \), final box quantization of \( v \) (reverse reaction);
3. QCFR box quantization in both ends, forward;
4. QCRF box quantization in both ends, reverse.

We have here introduced the same notation as in ref. [7]. The QCRF and QCFR methods should of course in the limit of an infinite number of trajectories give the same result, i.e., they obey detailed balance. In table 1 we show some reaction probabilities at two energies for forward and reverse reaction by the methods mentioned above. A total of 100–200 trajectories was used in each case. Table 1 shows large differences between the QCF and the QCR results and that the detailed balance is fulfilled for the QCFR and the QCRF method. The performance of the QCFR and the QCF methods are also visualized in figs. 1 and 2 where the reaction probabilities \( P_{v' \rightarrow v} \) \( (v' = 0, 1 \text{ and } 2) \) are shown. When comparing with quantum results (fig. 3) we see that the detailed struc-

![Fig. 1. Quasi-classical reaction probabilities \( P_{v' \rightarrow v} \) \( (v' = 0, 1, 2) \) for \( \text{H} + \text{Cl}_2 \) at 0.268 eV total energy. The QCFR (see text) method was used.](image1)

![Fig. 2. Quasi-classical reaction probabilities \( P_{v' \rightarrow v} \) \( (v' = 0, 1, 2) \) for \( \text{H} + \text{Cl}_2 \) at 0.268 eV total energy. The QCF (see text) method was used.](image2)
ture, which probably has its origin in the quantum behaviour of the vibrational degree of freedom, cannot be reproduced by classical trajectory calculations. Apart from this the agreement is however qualitatively correct. We also see that the QCFR calculation predicts the correct maximum at $v = 4$ in the $0 \rightarrow v$ case.

Since box quantization is a crude way of building in quantum principles in classical mechanics one would expect this quantization to be best for the most classical channel. Thus for the reaction $H + Cl_2 \rightarrow Cl + Cl$ the QCR method is expected to be superior because the $Cl_2$ vibrational energy spacing is smaller (the vibration is more "classical") than for HCl.$^{1}$ Table 1 actually confirms this ansatz but in

![Figure 3](image3.png)

Fig. 3. Quantum mechanical reaction probabilities $P_{v' \rightarrow v}$ ($v' = 0, 1, 2$) for $H + Cl_2$ at 0.268 eV total energy.

![Figure 4](image4.png)

Fig. 4. Quasi-classical QCFR reaction probabilities $P_{0 \rightarrow v}$ for $H + Cl_2$ as a function of total energy. The error bars indicate the statistical error associated with the Monte Carlo average.

![Figure 5](image5.png)

Fig. 5. Quantum mechanical reaction probabilities $P_{0 \rightarrow 0}$ for $H + Cl_2$ as a function of total energy.

ref. [7] exactly the opposite was found for the $F + H_2 \rightarrow FH + H$ reaction. Also here the QCR method was superior although the opposite could be expected. Thus it appears that no general rule can be given. Because of this and the automatic fulfilment of the principle of detailed balance we found it most convenient to use the QCFR method in the remaining part of this work. The QCFR method has for the $H + H_2$ reaction been used previously by Miller [15]. Although the threshold was lowered (see fig. 2 of ref. [15]) the QCFR method appeared to be inadequate for this system.

3. Results

Figs. 4–7 show the classical and the quantum mechanical reaction probabilities $P_{0 \rightarrow v}$ and $P_{1 \rightarrow v}$ for

![Figure 6](image6.png)

Fig. 6. Quasi-classical QCFR reaction probabilities $P_{1 \rightarrow 0}$ for $H + Cl_2$ as a function of total energy.
H. Essén et al./Collinear reaction rate constants for the H + Cl₂ and D + Cl₂ systems

Figs. 7 and 9 show the classical and quantum mechanical reaction probabilities $P_{0\rightarrow v}$ for H + Cl₂ and D + Cl₂, respectively. We note that the classical results are more "washed out", i.e., we get 2-3 dominating transitions (e.g., $P_{0\rightarrow 3}$ and $P_{0\rightarrow 4}$ in fig. 4) whereas the quantum mechanical calculations show just one dominating transition. The qualitative behaviour of the reaction probabilities is however the same. The most populated levels are classically predicted to be $v = 3, 4$ for HCl and $v = 4, 5, 6$ for DCl whereas we quantum mechanically get $v = 4$ for HCl and $v = 5$ for DCl and experimentally [16] $v = 2, 3$ for HCl and $v = 3, 4$ for DCl as most populated levels. The disagreement with experiment is however to be explained by the inadequacy of the collinear collision model. For instance it is shown in ref. [17] how the one-dimensional results, by three-dimensional considerations, can be modified to give agreement with experimental findings.

The total reaction probabilities $P_{R}^{R} = \sum_{v'} P_{v'\rightarrow v}$ for H + Cl₂ are shown as a function of the total energy in figs. 10 and 11. Here we get rather good agreement between the classical and the quantum mechanical results (except may be for $P_{2}^{R}$ and at energetic threshold). Thus the quantum effects are diminished when summing over quantum numbers.

4. Rate constants

The reaction rate constants are found from [7]:

Fig. 10. Total quasi-classical ACFR reaction probabilities $P_{R}^{R} = \sum_{v'} P_{v'\rightarrow v}$ for H + Cl₂ as a function of total energy.
Fig. 11. Total quantum mechanical reaction probabilities $P_v^R$ for H + Cl$_2$ as a function of total energy.

$$k_{uv}(T) = (2\pi k_B T)^{-1/2} \int_0^{e_m} \exp(-\beta e) \, \mathrm{d}e P_{uv}(e) \, e^{-\beta e}, \quad (1)$$

where $k_B$ is Boltzmann’s constant, $\beta = 1/k_B T$, $\mu$ the reduced collision mass and $e$ the kinetic energy.

We have calculated the total reaction rate constants $k_{uv}(T)$ to a given final vibrational state of HC1, i.e.,

$$k_{uv}(T) \equiv \sum_v f_v(T) k_{uv_v}(T). \quad (2)$$

Here we assume a Boltzmann distribution of the initial vibrational states, i.e.,

$$f_v(T) = \exp(-\beta E_v) \sum_v \exp(-\beta E_v), \quad (3)$$

where $E_v$ is the vibrational energy of Cl$_2$ in state $v$.

The rate constants $k_{uv}(T)$ are shown in an Arrhenius plot (fig. 12). The agreement between classical and quantum mechanical values is better than a factor of two for the individual $k_{uv}(T)$ rate constants and better than 10% for the total reaction rate constant $k(T) = \sum_v k_{uv}(T)$. This again shows how averaging over quantum numbers tends to wipe out the quantum effects.

5. Comparison with transition state theory

In this section we will compare the rate constants found numerically with values obtained by the Transition State (TS) theory. From the TS theory we get [18]

$$k_{TS}(T) = k_B T \frac{Q^*}{\hbar Q_T Q_{BC}} \exp(-E_0/k_B T),$$

where $\hbar$ is Planck’s constant, $E_0$ is the minimal energy necessary to reach the ground state of the activated complex i.e., $E_0 = E_b + E_b^\text{Cl} - E_b^\text{Cl}$. Here $E_b$ is the barrier height (0.1076 eV), $E_b^\text{Cl}$ and $E_b^\text{Cl}$ ground state energies of the complex H$^+$·Cl$^-$·Cl and Cl$_2$. The $Q$’s are partition functions for the complex ($Q^*$), translation of A ($Q_T$) and for Cl$_2$ ($Q_{BC}$). The vibrational energies of the transition state could now be calculated [11] and the partition function $Q^*$ could then be determined. We will however make the following simplifying assumptions

$$Q^* \approx Q_{BC} \quad \text{and} \quad E_0 \approx E_0^\text{BC}. \quad (4)$$

Since the H-atom is very light compared to the Cl-atom we imagine that the H-atom when colliding with the Cl-atom simply “hooks on” the Cl$_2$ molecule and acquires the momentum of the Cl-atom. In this way a vibrating complex HCl–Cl is formed and since we have an early barrier [6] we expect the potential in which this vibrator moves to be well approximated with the Cl$_2$ potential. Thus both the masses and the potential corresponds to what we have for Cl$_2$ and
and the assumptions in eq. (4) are justified.

For the one-dimensional translational partition function we have

\[ Q_T = \frac{(2\pi m_H k_B T)^{1/2}}{h}, \]

i.e.,

\[ k_{TS}(T) = \left(\frac{k_B T}{2\pi m_H} k_B T\right)^{1/2} \exp\left(-\frac{E_b}{k_B T}\right). \]  

(5)

The activation energy for the TS result is then

\[ E_a = -k_B \frac{d\ln k_{TS}}{d(1/T)} = E_b + \frac{1}{2} k_B T. \]  

(6)

This activation energy, which is 2.7–3.1 kcal/mol in the temperature range 200–600 K, is slightly larger than the 2.5 kcal/mol found from fig. 12. The lower activation energy found quantum mechanically could indicate that tunneling is important. Table 2 confirms this since tunneling is expected to be most important at low temperatures. Thus we get rate constants which are about a factor of two lower at 200 K whereas the agreement at 600 K is very good. The deviation of the TS results could of course also be due to the simplifying assumption made in eq. (4) or maybe more likely to the vibrational adiabatic (VA) approximation implicitly made in the TS model. The VA approximation has been investigated by Bowman et al. [19] for the H + H₂ reaction. In ref. [19] it was shown that the VA approximation in the transition state region was valid only in a restricted energy range.

The classical trajectory calculations yields also an activation energy of 2.5 kcal/mol. Since tunneling can be excluded in this case, the explanation is that the barrier has been lowered by the introduction of the initial box quantization.

We have also calculated the quantum mechanical rate constants for the reaction D + Cl₂ → DCI + Cl.

**Table 2**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( k(T) ) (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quantum mechanical</td>
</tr>
<tr>
<td>200</td>
<td>( 2.10 \times 10^2 )</td>
</tr>
<tr>
<td>300</td>
<td>( 1.47 \times 10^3 )</td>
</tr>
<tr>
<td>400</td>
<td>( 4.18 \times 10^3 )</td>
</tr>
<tr>
<td>500</td>
<td>( 8.05 \times 10^3 )</td>
</tr>
<tr>
<td>600</td>
<td>( 1.36 \times 10^4 )</td>
</tr>
</tbody>
</table>

**Table 3**

The isotopic quantum mechanical ratio \( k(H + Cl_2)/k(D + Cl_2) \) as a function of temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Isotopic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.58</td>
</tr>
<tr>
<td>250</td>
<td>1.48</td>
</tr>
<tr>
<td>300</td>
<td>1.45</td>
</tr>
<tr>
<td>350</td>
<td>1.42</td>
</tr>
<tr>
<td>400</td>
<td>1.41</td>
</tr>
<tr>
<td>450</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Table 3 shows the isotopic ratio \( k(H + Cl_2)/k(D + Cl_2) \) which approaches 1.4 at higher temperatures. This is also the ratio which one would get from the TS-model, i.e.,

\[ k_{TS}(H+Cl_2)/k_{TS}(D+Cl_2) = (m_D/m_H)^{1/2} \approx 1.4. \]  

(7)

6. Conclusions

The purpose of this paper was to investigate the performance of a classical mechanical description of a reactive system (H + Cl₂) which is much more "classical" (has smaller vibrational energy spacing) than the H + H₂, Cl + H₂ and F + H₂ systems which previously have been used for comparison between quantum and classical or semiclassical methods [1,5,7].

The symmetric QCFR method has been used here. The reason being that the principle of detailed balance then is properly fulfilled. Although it might be that the QCF or the QCR methods in certain cases could give better agreement with quantum mechanical calculations we feel that this would be fortuitous and have therefore preferred to use the "consistent" QCFR method.

It is found that often the detailed structure cannot be predicted by using the QCFR method. All qualitative features and even quantitative values of less detailed properties such as the total reaction rate constant are, however, predicted.

Acknowledgement

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adiabatic Transitions in Chemical Reactions" at CECAM, University of Paris, Orsay, France during summer 1975. The main part of this work was carried out there.

References