The effect of a potential well in the quasi-asymptotic region of a potential energy surface on the dynamics of the F + H\textsubscript{2} reaction

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Abstract

The effect of a potential well located in the quasi-asymptotic region of a potential energy surface for the F + H\textsubscript{2} reaction on the dynamics was investigated by carrying out quasi-classical trajectory and quantum-mechanical calculations for two similar potential energy surfaces differing only in the depth of the well. Results were obtained concerning cross sections, rate constants, vibrational branching ratios and differential cross sections. The results are discussed in relation to published results of calculations for the 6SEC potential energy surface and of experimental measurements.

1. Introduction

The reaction F + H\textsubscript{2} \rightarrow HF + H is of central importance in molecular dynamics. Numerous experimental and theoretical studies have been devoted to this reaction in recent years. The most critical element in the theoretical studies is the availability of a reliable potential energy surface (PES) to be used for the calculations. Over the years more and more accurate potential energy surfaces [1–8] have been developed for this reaction (for a summary see, for example, Ref. [9]). The two most accurate surfaces available today are the 6SEC PES of Truhlar and co-workers [7] and the SW PES of Stark and Werner [8]. These two surfaces reproduce the available experimental results reasonably well, but in general the calculated results for the SW PES are in better agreement with experiment.

Extensive quasi-classical trajectory (QCT) calculations for the 6SEC PES were carried out by Aoiz et al. [10–12] and by us [13]. We have also carried out quantum mechanical (QM) calculations of cross sections and rate constants for this PES [14]. Calculations of vibrationally state resolved differential cross sections [10] showed that while the results for F + H\textsubscript{2} are in general in reasonable agreement with experiment, the branching ratio $\sigma_\text{R}(\nu' = 3)/\sigma_\text{R}(\nu' = 2)$ is overestimated, the branching ratio $\sigma_\text{R}(\nu' = 1)/\sigma_\text{R}(\nu' = 2)$ is underestimated and the forward peak for $\nu' = 3$ is too large as compared to the experimental scattering results of Lee and co-workers [15,16]. The reverse trends were found for the SW surface [9,17]. As for rate constants, QCT calculations [13] for the 6SEC PES gave very good agreement with experiment [18–20] for F + D\textsubscript{2} over the whole temperature range of the calculations, but for F + H\textsubscript{2} the calculated rate constants were found to be lower than experiment, especially at low temperatures. QM calculations [14] showed that quantum effects are not significant for the 6SEC PES and therefore the dis-
crepancy between the calculated and experimental rate constants for F + H₂ is nearly the same as for the QCT results. QM calculations for the SW PES [21,22] gave good agreement with experimental rate constants [18–20] for F + H₂ and for F + D₂ at high temperatures, but somewhat too high values at low temperatures.

In a recent paper [14] we have suggested that a PES similar to the 6SEC PES, but with a shallow potential well located in the quasi-asymptotic region, may give higher rate constants than those calculated for the 6SEC surface leading to a better agreement with experiment. The goal of the present study was to examine the effect of such a well on the dynamics. This was achieved by carrying out calculations employing two potential energy surfaces which are very similar, except for the depth of the well in the quasi-asymptotic region. These are the 5SEC [5] and 5SEC-W [6] surfaces developed by Truhlar and coworkers, having wells with depths (spherically averaged) of 0.145 kcal/mol and 0.625 kcal/mol, respectively. It should be noted that the 6SEC PES is very similar to the 5SEC PES, except for a higher adiabatic barrier for the formation of HF (v' = 3) and therefore conclusions derived from the present study are also relevant to the 6SEC PES. Most of the calculations were carried out by the QCT method. Some QM calculations were also performed. The results of these calculations are presented and discussed in the following sections.

2. Results and discussion

2.1. QCT calculations

2.1.1. Cross sections and rate constants

Cross sections as a function of collision energy for F + H₂ and F + D₂ were calculated for thermal distributions of rotational states at four temperatures in the range 200–500 K, employing the 5SEC and 5SEC-W surfaces. The computation procedure was similar to the one used in our earlier QCT study [13]. For every collision energy 10000–30000 trajectories were calculated. The results for 200 K are presented in Fig. 1.

As can be seen from Fig. 1, the cross sections for the two surfaces are rather similar except for the low-energy range, which is the most important range for calculating rate constants. In this range the cross sections for the 5SEC-W PES are significantly higher than for the 5SEC PES. The threshold energy is lower for the 5SEC-W PES than for the 5SEC PES by about 0.5 kcal/mol. The higher reactivity for the 5SEC-W PES can probably be attributed to attractive forces due to the potential well which are most effective for collisions with low velocities and small impact parameters and lead to longer collision times and higher reaction probabilities. These forces become less effective with the increase in collision energy. This explanation is supported by the examination of individual trajectories for the two potential energy surfaces.

The calculated cross sections were used for calculating rate constants, which are presented in Table 1. As can be seen, the rate constants for the 5SEC-W PES are higher than for the 5SEC PES and this could be expected considering the results for the cross sections. The largest differences are observed for the lowest temperature for which the weight of the low collision energies is the most significant. The results in Table 1 indicate that the presence of a well increases the rate constants for the F + D₂ reaction to the same extent as for the F + H₂ reaction. Thus, the present QCT calculations indicate that a PES similar to the 6SEC PES, but with a potential well in
Table 1
Rate constants for the reactions $\text{F} + \text{H}_2$ and $\text{F} + \text{D}_2$ for the potential energy surfaces 5SEC and 5SEC-W

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>5SEC</th>
<th>5SEC-W</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{\text{F} + \text{H}_2}$</td>
<td>$k_{\text{F} + \text{D}_2}$</td>
</tr>
<tr>
<td>200</td>
<td>0.54</td>
<td>0.34</td>
</tr>
<tr>
<td>298</td>
<td>1.55</td>
<td>1.03</td>
</tr>
<tr>
<td>400</td>
<td>2.70</td>
<td>1.86</td>
</tr>
<tr>
<td>500</td>
<td>3.77</td>
<td>2.62</td>
</tr>
</tbody>
</table>

*aUnits of $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.
*bKinetic isotope effect $k_{\text{F} + \text{H}_2} / k_{\text{F} + \text{D}_2}$.

the quasi-asymptotic region, will not give results in better agreement with experimental rate constants than those obtained for the 6SEC PES. It may improve the agreement for the $\text{F} + \text{H}_2$ reaction but at the same time spoil the good agreement obtained for the $\text{F} + \text{D}_2$ reaction.

2.1.2. Vibrational branching ratios

Vibrational branching ratios $\sigma_R(v' = 3) / \sigma_R(v' = 2)$ and $\sigma_R(v' = 1) / \sigma_R(v' = 2)$ for the $\text{F} + \text{H}_2$ reaction for the 5SEC and 5SEC-W potential energy surfaces are shown in Fig. 2 (rotational temperature 200 K). As can be seen, the presence of the deeper potential well in the 5SEC-W PES causes a decrease in the ratio $\sigma_R(v' = 3) / \sigma_R(v' = 2)$ and an increase in the ratio $\sigma_R(v' = 1) / \sigma_R(v' = 2)$. As mentioned in the introduction, such trends are needed in order to improve the agreement between calculations for the 6SEC PES and experiment. These changes are probably due to attractive forces of the well, which cause a decrease in the effective impact parameter as the reagents approach each other, leading to the formation of products with less vibrational energy, because the new F–H bond is formed less stretched. Such a correlation between the amount of vibrational energy in the new F–H bond and the impact parameter was observed from the examination of average properties of groups of trajectories with different impact parameters.

2.1.3. Differential cross sections

Vibrational state selected differential cross sections for the $\text{F} + \text{H}_2$ reaction for the collision energies 1.0 and 3.42 kcal/mol are shown in Fig. 3 (rotational temperature 200 K). As can be seen from the figure, for the lower collision energy, which is close to the threshold energy, the scattering is mainly backwards, as might be expected for such reactive collisions which are associated with small impact parameters. The cross sections for the 5SEC-W PES are significantly larger than the corresponding ones.
for the 5SEC PES. For the higher collision energy some forward scattering is observed. The values for the two surfaces are rather similar, but the forward peaks for the 5SEC-W PES are somewhat lower than for the 5SEC PES. This can probably be attributed to the attractive effect of the potential well, which causes a decrease in the effective impact parameter as the reagents approach each other, resulting in less forward scattering. This finding is consistent with the results concerning the vibrational branching ratios discussed above (Fig. 2). Such a change is in the direction needed in order to improve the agreement between calculations for the 6SEC PES and experiment.

2.2. QM calculations

As shown above, the presence of a well in the quasi-asymptotic region has no influence on the quasi-classical kinetic isotope effect (KIE): the ratio $k_{F+H_2}(5SEC-W)/k_{F+D_2}(5SEC-W)$ has nearly the same value as the ratio $k_{F+H_2}(5SEC)/k_{F+D_2}(5SEC)$ over the whole temperature range of the calculations (see Table 1). The effect of the well was also investigated by some limited QM calculations.

The QM method and procedure were the same as those used by us in earlier QM studies [14,21-23]. According to this method the Schrödinger equation was solved in the reagents arrangement channel employing negative imaginary potentials (NIPs) [24-30], and the calculations were done within the $J_z$ (coupled-states) approximation [31,32].

Cross sections as a function of collision energy for the reactions $F + X_2(v = j = 0) \rightarrow XF(all) + X$ ($X = H$ or $D$) for the 5SEC and the 5SEC-W surfaces are presented in Fig. 4. As can be seen from Fig. 4, for both isotopic analogs, the van der Waals well caused the appearance of quantum resonances in the threshold region. It seems that the existence of the well provided conditions for Feschbach-type resonances [33-35], which enhanced the tunneling processes. These processes seem to be more pronounced in the case of $F + H_2$ than in the case of $F + D_2$, indicating a larger increase in $k_{F+H_2}$ than in $k_{F+D_2}$ and thus an improvement in the agreement between the calculated and the measured kinetic isotope effect, $k_{F+H_2}/k_{F+D_2}$.

3. Conclusions

The effect of a potential well in the quasi-asymptotic region of a potential energy surface for the $F + H_2$ reaction on the dynamics has been investigated by QCT and QM calculations and the results were discussed in relation to results of calculations for the 6SEC PES and of available experimental data. The main conclusions from the QCT study concerning the effect of the well are:

(a) Threshold energies are lowered, cross sections for low collision energies are increased and rate constants are also increased. The effects were found to be similar for the reactions $F + H_2$ and $F + D_2$ and to increase with decreasing temperature. The similar increase in rate constants for the $F + H_2$ and $F + D_2$ reactions indicates that the presence of a well will not improve the agreement between calculated kinetic results for the 6SEC PES and experiment. It may improve the agreement between calculated and experimental rate constants for $F + H_2$ but at the same time spoil the agreement for the $F + D_2$.

(b) The branching ratio $\sigma_R(v' = 3)/\sigma_R(v' = 2)$ decreases, the branching ratio $\sigma_R(v' = 1)/\sigma_R(v' = 2)$ increases and the forward peak for the product HF ($v' = 3$) is lowered. These changes are in the direc-
tion needed in order to improve the agreement between results of calculations for the 6SEC PES and experiment.

The limited QM calculations carried out in the present study showed that a potential well in the quasi-asymptotic region causes the appearance of quantum resonances near the threshold energy. They seem to be higher for \( \text{F} + \text{H}_2 \) than for \( \text{F} + \text{D}_2 \), indicating larger changes in rate constants for \( \text{F} + \text{H}_2 \) than for \( \text{F} + \text{D}_2 \) and thus an improvement in the agreement between results of calculations for the 6SEC PES and experiment. More detailed QM calculations are needed in order to reach quantitative conclusions concerning the effect of these resonances on the rate constants. It would be of much interest to carry out such calculations for a PES similar to the 6SEC PES but with a deeper potential well in the asymptotic region.

References