The Dynamics of the $S(^1D)$+H_2/D_2 Reactions at Low Temperature via Statistical Simulations

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Abstract

Two different statistical approaches, the statistical quantum model (SQM) and the mean potential phase space theory (MPPST), have been employed to calculate the integral cross sections for the reactive collisions between $S(^1D)$ and H_2/ D_2 in the low energy regime (below 0.3 eV collisional energy). The rate constant for the $S(^1D) + H_2 \rightarrow SH + H$ reaction has been also obtained and compared with previously reported experimental and theoretical results. The good agreement shows the capability of these two methods to study the dynamics of these complex-forming atom-diatom processes in the present energy regime.

Keywords: Reaction dynamics, statistical methods, atom-diatom collisions

1. Introduction

Following the pioneering experiments by Lee and Liu [1-3], the dynamics of the $S(^1D)$+$H_2 \rightarrow$ SH+H reaction and its corresponding isotopic variants, with substitutions of H atoms by D, have been investigated in some detail by means of kinetics and crossed molecular beam (CMB) experiments [4-7] at very low temperature (down to $\approx$ 6 K) and energy ($\approx$ 0.5 meV). Those studies were accompanied by time independent exact quantum mechanical (EQM) calculations performed on the *ab initio* potential energy surface (PES) for the ground electronic state $^1A'$ reported in Ref. [8]. The presence of a deep potential well

($\approx$ 4 eV) between reactants and products suggests the existence of an intermediate SH_2 complex supporting a number of bound and resonance states. In fact, many authors have concluded that the overall dynamics of the reaction is ruled by this complex-forming mechanism [3, 9, 10], which warrants the use of statistical techniques to investigate the process [3, 7, 11-17]. In this sense, we present in this work results of calculations performed with the statistical quantum model (SQM) [13, 14, 18] and the mean potential phase space theory (MPPST) [19, 20]. This combined theoretical investigation at the low energy regime is in-line with the recently reported study on the $C(^1D)$+H_2 reaction and isotopic variant [21]. Integral cross sections (ICS) below 10 meV both

for the S(^1D)+H$_2$ and S(^1D)+D$_2$ reactions are compared with the EQM results and the CMB measurements reported in the above mentioned recent literature. In addition, cross sections are also calculated at larger values of the collision energy (0.2 eV) in order to compare with previous excitation functions by Lee and Liu [2]. Rate constants up to 300 K have been obtained with the SQM and MPPST and compared with results reported in the existing literature.

In Section 2 basic details of both theoretical methods are shown; in Section 3 results are presented and discussed and finally, in Section 4 we present the conclusions.

2. Methods

2.1 Statistical Quantum Method

The theoretical basis of the SQM have been presented elsewhere before [13, 14] so here we will only give some details. Under the assumption of a complex-forming dynamics for the atom-diatom reaction, the state-to-state probability $P_{i \to f}$ between an initial state i of the reactant diatom and a final f state for the product diatom can be approximated as the product $P_{i \to f} = p_i\, p_f\, /\, \sum_j\, p_j$ between the capture probability of the intermediate complex to form from the initial state, p_i, and the probability to fragmentate into the final state, p_f, divided by the sum of the individual probabilities corresponding to all energetically available rovibrational states. The calculation of such probabilities is performed separately in each arrangement between the corresponding asymptotic region and a so-called captured radius defining the region in which the complex is supposed to form by solving the coupled-channel equations by means of a time independent log derivative propagation of the wave function [13].

The state-to-state probability is employed to calculate the ICS as $\sigma_{ij}(E) = A_i \sum_J (2J+1)P^J_{if}(E)$,

where $A_i = \pi\, \hbar^2\, /\, [(2j+1)\, \mu^2\, (E - E_{vj})^2]$, being j the rotational state of the reactant diatom, E_{vj} is the energy of the rovibrational H$_2$(v,j) state and μ is the reduced mass of the system. The Boltzmann average of this ICS in terms of the collision energy yields the rate constant [21].

2.2 Mean Potential Phase Space Theory

The MPPST is a semi-classical technique to tackle the study of barrierless reactions [19, 20] assuming as well the formation of an intermediate complex. In this case, the individual probabilities for the asymptotic semiclassically quantized *(v; j)* states are calculated following an approximate two-body capture model [22] which accounts for tunnelling by means of the WKB model [23] through the radial effective potential. The interaction potential is averaged over the Jacobi angle to implicitly account for moderate anisotropies involved in complex-formation dynamics for barrierless processes at low collision energies. Here, a rigid rotor anharmonic oscillator approximation is considered to treat internal states of both reactant and product channels. The capture cross sections resulting from the isotropic assumption for the inter-fragment (averaged) potential do not depend on the initial rotational state of the reactant diatom.

The SQM calculations are performed using the PES by Ho *et al.* [8]. MPPST predictions have been obtained, in turn, considering also the matching with long range terms described in Ref. [24]. All calculations have been performed for the ground rovibrational states, H$_2$($v = 0$, $j = 0$) and D$_2$($v = 0$, $j = 0$), respectively.

3. Results and Discussion

The SQM and MPPST methods described in the previous section have been employed to calculate ICS for the S(^1D)+H$_2$ → SH+H reaction

between 10^{-4} eV and 10^{-2} eV which are compared in Figure 1 (see inset) with the EQM results and CMB measurements of Refs. [5, 6]. Present theoretical cross sections are absolute values and no scaling factor are needed in the comparison with EQM results. Experimental excitation functions, on the contrary, have been scaled to match the SQM predictions at a single energy. The comparison reveals that both statistical cross sections nicely reproduce the trend of the measured excitation functions in the very low energy regime, where the ICS display the expected decreasing behavior with energy in a barrierless reaction. It is worth noticing how, in particular, the SQM approach manages such a good accord even if the long range behavior of the PES is not included in the calculation. Some deviation with respect to SQM and MPPST results is observed in the EQM cross sections when the energy decreases sufficiently.

In an attempt to extend the comparison with experimental values reported in Ref. [2], present theoretical calculations have been extended well above ≈ 10^{-2} eV, the largest collision energy considered in the study of Refs. [5, 6]. The obtained ICSs for the entire energy range are shown in Figure 1 (main panel). The agreement between the SQM and MPPST cross sections and excitation functions measured in the experiment by Lee and Liu is remarkably good, thus suggesting that the statistical descriptions provided by these two techniques are capable to reproduce the experimental information over a wide energy regime.

A similar calculation for the $S(^1D)+D_2$ reaction yields ICS for collision energies between ≈ 10^{-4} eV and 0.3 eV. In particular, the comparison between cross sections here obtained with the SQM and the MPPST and EQM results from Ref. [7] up to 0.02 eV is shown in detail in Figure 2. As in the

case of the collision with H_2, the SQM predictions are between the exact and MPPST cross sections. Excitation functions for $S(^1D)+D_2$ reported in Ref. [2] have been scaled with the same factor employed in Figure 1 for the case of $S(^1D)+H_2$ and compared with the present theoretical results. Differences between theory and experiment are noticeable at this larger energy range. Nevertheless, it is worth mentioning that some of the conclusions extracted from the isotopic investigations of the title reaction by Lee and Liu have been subject to discussion. The authors found themselves surprising the trend followed by the ICSs measured for the $S(^1D)+HD$, $S(^1D)+H_2$ and $S(^1D)+D_2$ reactions: σ (HD) > $\sigma(D_2)$ > σ (H_2) [2]. Moreover, quasi-classical trajectory (QCT) [9, 25, 26] and capture model calculations were not able to reproduce the isotope effect and H_2/D_2 ratios seen in experiments [1, 2, 3].

In Table 1 ratios between the cross sections for the $S(^1D)+H_2$ and $S(^1D)+D_2$ reactions obtained with the SQM and MPPST methods are compared for low energies (< 0.02 eV) with the EQM of Ref. [7] and at higher values of the collision energy (> 0.03 eV) with the measured excitation functions of Lee and Liu [2]. Both statistical approaches predict values around 1, which slightly overestimate the EQM results. As expected, the comparison with the experimental cross sections reveals the marked differences mentioned above.

11

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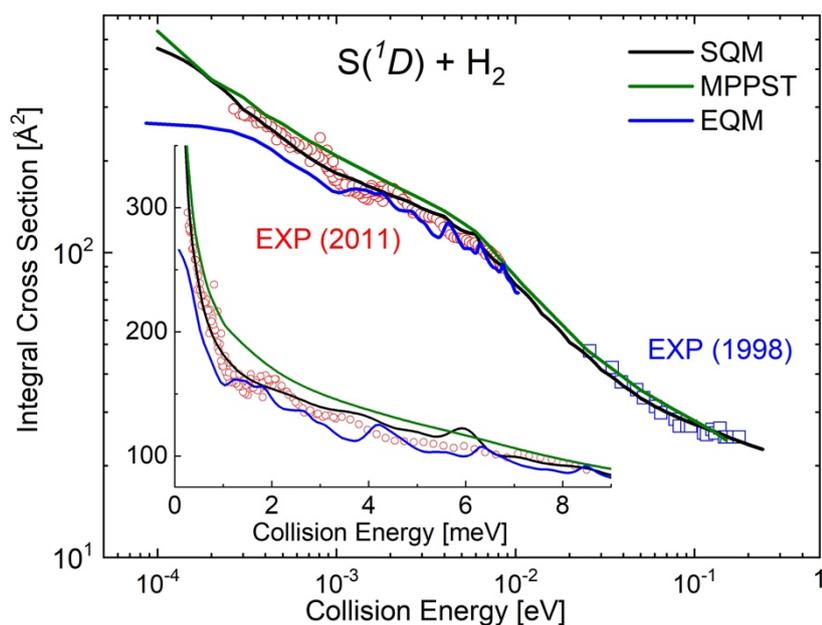
Figure 1 - ICS (in Å^2) for S(^1D)+H$_2$ as a function of the collision energy in a double-logarithmic scale: Experimental (empty red circles) and EQM (blue line) results from Refs. [5, 6], experimental excitation functions by Lee and Liu [2] at high energies (in blue squares) and MPPST values (in green line) from Ref. [12] (here extended up to 0.8 eV) are compared with present SQM (red line) predictions. Inset shows comparison up to 8 meV. Experimental results have been scaled separately for the comparison with the theoretical cross sections.
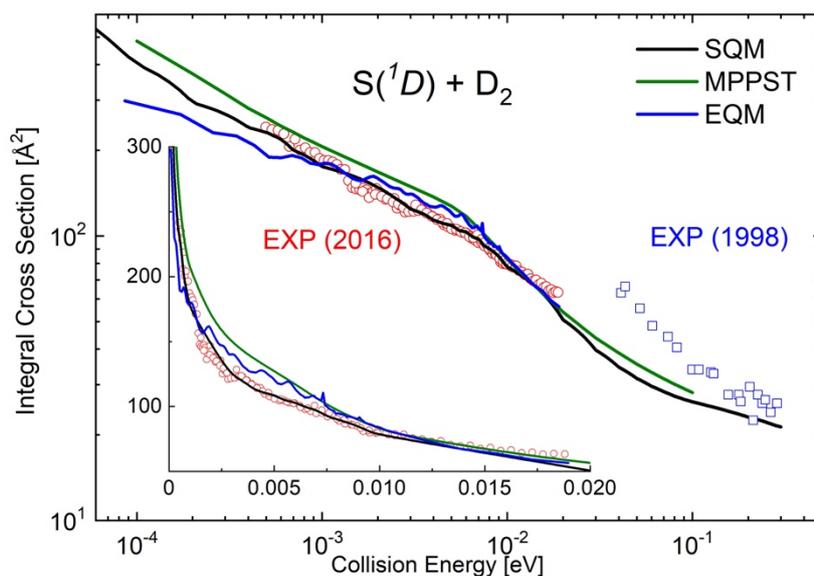
Figure 2 – Same as Figure 1 for the S(^1D)+D$_2$ reaction. Present SQM predictions (black line) are compared with EQM (blue line), MPPST (green line) and experimental (open red circles) results from [7] and excitation functions reported in Ref. [2] (open blue squares). The inset shows the comparison up to 0.02 eV. MPPST have been calculated for this work up to 0.1 eV.

12

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Table 1. Ratio between the ICSs for the S(^1D)+H$_2$ and S(^1D)+D$_2$ reactions at specific values of the collision energy (in eV) obtained with the SQM (second column) and MPPST (third column) approaches in comparison with those adapted from the EQM cross sections of Ref. [7] (in fourth column) and the experimental values of Ref. [2] (in the last column).

Energy [eV]	SQM	MPPST	EQM	EXP
5 10^{-4}	1.026	1.015	1.065	
10^{-3}	1.038	1.006	0.871	
5 10^{-3}	1.095	0.989	0.874	
0.01	1.009	1.006	0.885	
0.05	1.053	0.998		0.591
0.08	1.056	1.002		0.667
0.1	1.048	0.997		0.783

Recent studies on the S(^1D)+H$_2$ reaction [5, 6] also included the calculation of the rate constant at temperatures between 5.8 and 298 K. In Figure 3 we show the actual comparison of present SQM and MPPST rates with those reported in Ref. [5] and rates obtained in a ring polymer molecular dynamics (RPMD) calculation [27]. Both the SQM and MPPST approaches yield predictions in a remarkably good agreement with the measured rates at 23 and 49 K [5]. As the temperature increases, the SQM constants compare quite well with the EQM results and lie slightly below the measurements and the RPMD values with which MPPST compares perfectly. Figure 3 also includes the mean potential capture theory (MPCT) predictions corresponding to the capture theory approximation version of the MPPST developed in Ref. [12], which reproduce nicely the experiment and remain just above the RPMD calculations. In MPCT, reaction probability is supposed to be unity given the process exothermicity so that the reaction cross section equals the complex forming cross section. Besides, small differences are observed between the MPPST and MPCT rates because of the classical treatment of the orbital angular momentum and the neglect of tunnelling in the latter approach. MPPST cross sections are higher than the SQM results, a possible consequence of a larger attraction of the long range terms from Ref. [24] included in the MPPST calculation.

The only noticeable discrepancies between theory and experiment are seen at the lowest temperatures, where the reported measurements at T = 5.8 K (perhaps those with the largest uncertainty in Ref. [5]) are clearly overestimated by the theoretical counterparts. Rate constants calculated with the time dependent version of the SQM approach [17] do not differ too much from those reported here.

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13

Present results are indication of the good performance of both the SQM and MPPST approaches to describe the capture dynamics of the S(^1D)+H$_2$ reaction. Previous applications of these techniques to reproduce both EQM [28] and experimental [2] angular distributions, product translational energy distributions and rotational cross sections [18] confirmed, on the other hand, the complex-forming mechanisms which seem to govern the overall dynamics of the process up to ≈ 0.2 eV.
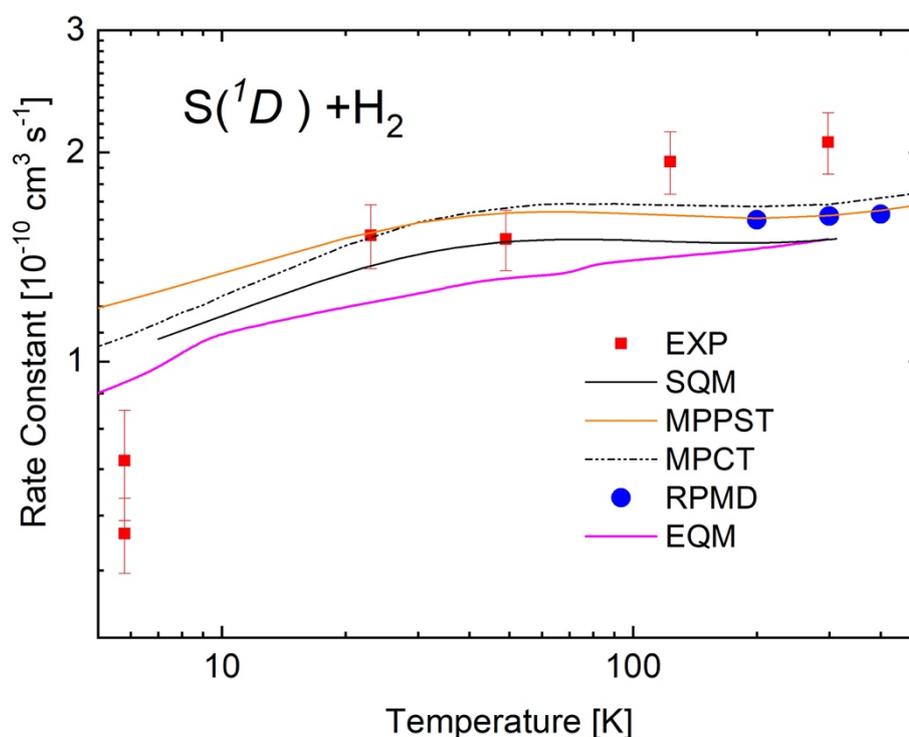
Figure 3 - Rate constants as a function of the temperature between 5 K and 300 K for the S(^1D)+H$_2$ reaction. Present SQM (black solid line) and MPPST (orange solid line) results are compared with EQM (magenta line) [5], RPMD (blue circles) [27], MPCT (black dashed line) [12] and experimental (red squares) [5] results.

4. Conclusions

The statistical quantum model (SQM) and the mean potential phase space theory (MPPST) have been applied to calculate integral cross sections (ICSs) for the S(^1D)+H$_2$ and S(^1D)+D$_2$ reactions. Comparison with recent exact quantum mechanical results and crossed molecular beam measurements at low energies (< 8 meV) reveals a fairly good agreement. The extension to a larger energy regime (up to ≈ 0.3 eV) shows a remarkable accord with experimental excitation functions for the case of H$_2$ but differences are noticeable in the case of collisions with D$_2$ in consistence with previously reported theory versus experiment discrepancies observed for isotope effects and ratios. Calculated rate constants between 5 and 300 K compare reasonably well too with experimental values and previous results obtained by means of a ring polymer molecular dynamics approach. Both the SQM and MPPST are then found to provide a satisfactory capture dynamics of the title.

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15

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16

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