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Statistical investigations of the $S(^1D)+HD$ reaction at the low energy range ^{*}

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Abstract

The dynamics of the $S(^1D)+HD$ reaction has been investigated at the low energy regime by means of a statistical quantum method and mean potential phase theory. Statistical predictions for cross sections down to 10^{-4} eV and the corresponding isotope branching ratios have thus been calculated and compared with previous results from the literature. Integral cross sections are also extended up to 0.2 eV to compare with experimental excitation functions reported in the past. Differences between theoretical and experimental branching ratios between the two possible product channels, $SD+H$ and $SH+D$, are observed.

1. Introduction

In the past years a lot of work has been devoted to investigate in detail the dynamics of the $S(^1D)+H_2$ reaction and isotopic variants in which one or both hydrogen atoms are substituted by deuterium. The pioneering work by Lee and Liu [1, 2, 3, 4] has been recently completed with further kinetics and crossed molecular beam (CMB) measurements which have provided valuable information on these reactions at very low temperature (down to $T \approx 6$ K) and collision energies ($E_c \approx 0.5$ meV) [5, 6, 7, 8]. These experimental investigations were accompanied with theoretical calculations of integral cross sections (ICSs) and rate constants by means of an time independent (TI) exact quantum mechanical (EQM) method employing the potential energy surface (PES) by Ho *et al.* [9]. The $S(^1D)+HD$ reaction, in particular, was the subject of the study by Lara *et al.* [8] in which ICSs for both product arrangements, $SD + H$ and $SH + D$, obtained through a CMB experiment were reported between 0.46 meV and 16 meV. The comparison with the above mentioned TI EQM calcula-

tions including accurately described long-range interactions [10] revealed that the theoretical results failed to reproduce both the product branching ratio and the resonancelike features observed in the $SH+D$ channel. The inclusion of excited PES for a proper nonadiabatic treatment was suggested as a possible solution.

This branching ratio or intramolecular isotope effect defined as $\sigma_{SD+H}/\sigma_{SH+D}$ is one of the most commonly analyzed issues in this process. According to the measurements performed by Lee and Liu [1, 3, 4], such SD / SH ratio remains almost constant around 0.7 over the entire energy range between 0.026 and 0.26 eV. This value was slightly smaller than previous experimental reports by Ianagaki *et al.* [11] (0.9 ± 0.1) and Tsukiyama *et al.* [12] (1.91 ± 0.10). The branching ratio between both product channels were found to oscillate around ~ 1 as a function of the energy both in the time dependent EQM calculation by Yang *et al.* [13] and in the quasi-classical trajectory (QCT) calculation by Bañares *et al.* [14]. Authors of Ref. [14], which also found differences between the measured isotope effects and predictions of a capture model, pointed out the detection method employed in the experiment as a possible explanation for the strong disagreement with theoretical results. That would also solve the issue regarding the surprising trend followed by the excitation functions measured for the

^{*}This letter is dedicated to Prof. Fernando Pirani in the occasion of his retirement

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three reactions: $\sigma_{\text{HD}} > \sigma_{\text{D}_2} > \sigma_{\text{H}_2}$, which consequently yield an unexpected sequence for the corresponding thermal rate constants [1]. The QCT investigation carried out by Chao *et al.* [15] on the PES of Ref. [16] led however to larger SD/SH ratios, which fluctuates between 1.2 at $E_c = 0.02$ eV and 0.2 eV, respectively, which also overestimate the results reported in the experiment by Lee and Liu.

Many authors have concluded that the overall dynamics of the collision between $\text{S}(^1D)$ and molecular hydrogen correspond to an insertion mechanism involving the formation of an intermediate complex [4, 16, 17]. Such a possibility has encouraged the application of statistical techniques, such as phase space theory (PST) [3, 4, 7, 18, 19], a collision complex theory [20] and versions of the statistical quantum method (SQM) developed by Manolopoulos and coworkers [22, 23, 24, 25, 26, 27] to study the $\text{S}(^1D)+\text{H}_2$ reaction and its different isotopic variants. Among the efforts to reproduce the recent information about these reactions at the low energy and temperature regime with this sort of theoretical methods such as a semi-classical capture model [18, 7] and the mean potential phase space theory (MPPST) [19], only the approach by Grozdanov and McCarroll [28] was specifically applied to the $\text{S}(^1D)+\text{HD}$ reaction.

As in our previous study on the $\text{C}(^1D)+\text{H}_2/\text{D}_2/\text{HD}$ reactions [29], and completing our previous report on the collisions with H_2/D_2 reactions [30] in this work we perform an investigation of $\text{S}(^1D)+\text{HD}$ by means of the already mentioned SQM and MPPST techniques. In an attempt to compare the dynamics for both product channels, $\text{SD}+\text{H}$ and $\text{SH}+\text{D}$, we extend the energy range under study to cover from the cold regime around 10^{-4} eV studied in the recent CMB experiments up to 10^{-1} eV, the energy range investigated by Lee and Liu in their measurements. Special emphasis will be made on the possible evolution of isotope branching ratios as a function of the energy, comparing the present statistical predictions with existing results from the literature.

The structure of the paper is the following: In Section 2 details of the two statistical approaches employed in this work are given; results are shown and discussed in Section 3 and finally conclusions are in Section 4.

2. Theory

The SQM calculations are performed using the PES by Ho *et al.* [9]. MPPST predictions have been obtained, in turn, considering the matching with long range terms described in Ref. [10]. The calculations have been performed for the ground rovibrational $\text{HD}(v=0, j=0)$ state

2.1. Statistical Quantum Method

Under the assumption that the reaction proceeds via the formation of an intermediate species, the SQM proposes the following expression for the state-to-state probability [22, 21]:

$$P_{vj,v'j'}^J(E) \simeq \frac{p_{vj}^J(E)p_{v'j'}^J(E)}{\sum_{v''j''} p_{v''j''}^J(E)}, \quad (1)$$

where $p_{vj}^J(E)$ and $p_{v'j'}^J(E)$ are, respectively, the capture probabilities for the formation from the initial diatomic rovibrational state (v, j) and fragmentation of the collision complex onto the final (v', j') state at the total angular momentum J and the energy E , and the indexes in the sum of the denominator, $v''j''$, run over all the energetically open rovibrational states both in reactants and products. In Equation (1) the sum in the denominator runs for all rovibrational states energetically accessible at E . The calculation of those individual probabilities is performed with a TI approach under the centrifugal sudden approximation using a log derivative propagation between a capture radius R_c and an asymptotic distance R_{max} . The values of these radii for both the reactant and products arrangements are shown in Table 1.

The reaction probability of Equation (1) is employed to calculate ICSSs, $\sigma_{vj,v'j'}(E)$, as follows:

$$\sigma_{vj,v'j'}(E) = \frac{\pi}{k_{vj}^2(2j+1)} \sum_J (2J+1) P_{vj,v'j'}^J(E), \quad (2)$$

where $k_{vj}^2 = 2\mu(E - E_{vj})/\hbar^2$, with E_{vj} as the energy of the initial rovibrational state of the reactant diatom and μ the reduced mass of the system.

Table 1: Values for parameters of the SQM calculation: Capture radius R_c (in Å), asymptotic radius R_{max} (in Å) and maximum value of the total angular momentum J_{max} at the largest collision energy here considered, 0.3 eV.

	R_c	R_{max}	J_{max}
S + HD	1.85	33.45	59
SD + H	3.12	43.69	57
SH + D	2.24	31.38	59

2.2. Mean Potential Phase Space Theory

The other statistical approach employed in our study, the MPPST, is a semi-classical technique to tackle the study of reactions governed by long-range forces [31, 32] assuming as well the formation of an intermediate complex. In Equation (1), we obtain individual probabilities for the asymptotic semiclassically quantized (v, j) states following an approximate two-body capture model [33] which gives account for the tunnelling by means of the WKB model [34] through the averaged radial effective potential over the reactant γ Jacobi coordinate. Such an averaging also implicitly takes into account the moderate anisotropies involved in complex-formation dynamics for barrierless processes at low collision energies. In this case, a rigid rotor anharmonic oscillator approximation is considered to treat internal states of both reactant and product channels [35]. The capture cross sections produced after the isotropic assumption for the inter-fragment potential do not depend on the initial rotational state of the reactant diatom.

3. Results

The ICSs for the title reaction calculated by means of the present SQM and MPPST methods are shown in Fig. 1 in a double logarithmic scale compared with the EQM and experimental results from Ref. [8]. The agreement with the measured excitation functions for both product arrangements is relatively good at some energies, but the statistical predictions exhibit some different dependence with the collision energy E_c . Thus, for example, cross sections for SD+H and SH+D are clearly separated at the entire energy range here considered. They do not cross as the EQM results suggest at low energy ($\approx 2 \times 10^{-4}$ eV) or get close as manifested by the experiment beyond ≈ 0.03 eV. Both SQM and MPPST approaches reproduce reasonably well the experimental ICS for the SD-forming process, but the same can not be said for the other product channel, especially as the energy increases beyond $E_c \approx 7 \times 10^{-3}$ eV. In turn, the comparison with the EQM results reveals the opposite: a fairly good description (although slightly smaller) of the ICS for the SH+D channel at almost the entire energy range under consideration and a poor performance to reproduce the cross section for the SD-forming channel at the lowest energies (below $\approx 10^{-3}$ eV). Similar difficulties to provide an overall reproduction of the hyperspherical coordinates calculation

Figure 1: ICSs (measured in $\text{\AA}^2$) for the reaction $S(^1D) + HD$ as a function of the energy (measured in eV) obtained with present SQM (red lines) and MPPST (blue lines) calculations in comparison with EQM (black lines) and experimental (open symbols) results reported by Lara *et al.* [8]. Theoretical results for the SD + H (SH + D) product channel are represented by solid (dashed) lines and measurements are shown with green squares (magenta circles). Measured ICSs have been scaled with the same factor for both product channels in the comparison with the theoretical values.

and measurements reported by Lara *et al.* [8] for both product arrangements were found in the study of the $S(^1D)+HD$ reaction performed by Grozdanov and McCarroll [28].

Interestingly some of those differences remain when the comparison is established for the total process $S(^1D)+HD$ summing both product arrangements together. Fig. 2 shows the theoretical cross sections obtained with present statistical techniques besides the experimental excitation functions reported in Refs. [8] and [1] and the EQM by Lara *et al.* [8]. The trend exhibited by the sum of the measured contributions from the SD and SH forming channels oscillates around the line in common followed by the three theoretical approaches beyond 10^{-3} eV. The EQM ICS, on the other hand, differ quantitatively from both statistical predictions below that precise collision energy, but as the energy increases it matches nicely first the SQM cross sections up to 4×10^{-2} eV, and then the MPPST result. There is no however any indication of deviation from the trend followed by the statistical cross sections as the energy decreases, as opposed to the $S(^1D)+H_2$ and $S(^1D)+D_2$ cases [30]. The excitation functions from Lee and Liu's measurements [1] look consistent with the recent experimental information on the $S(^1D)+HD$ reac-

Figure 2: Comparison between the total ICS for the reactions $S(^1D) + HD$ summed for both $SD + H$ and $SH + D$ product channels obtained in the present SQM (black line) and MPPST (magenta line) calculations and experimental results reported in Refs. [8] (red squares) and [1] (blue circles).

tion provided at a lower energy regime [8] and, in addition, is nicely well reproduced by the statistical techniques, especially the SQM approach.

Fig. 3 summarizes the information we have regarding the $[SD+H] / [SH+D]$ ratio between the two possible product channels of $S(^1D) + HD$. Present results obtained by means of the SQM and MPPST methods are compared with the EQM and experimental ratios estimated from the results reported in Ref. [8] and with those shown in the study by Lee and Liu [1]. The statistical predictions are clear and consistent in indicating the preference for the SD-forming channel (more than twice the output seen through the $SH+D$ option) for most of the energy range under consideration. They only exhibit a sudden decrease as the collision energy gets close to 0.1 eV but never below 1, as ratios reported at this higher energy regime (between 4×10^{-2} and 0.25 eV) in Ref. [1]. These experimental data, firmly established around 0.75, might be interpreted as the extrapolation of those obtained from the more recently reported investigation performed by Lara *et al.* [8] according with the decreasing values of the ratio from 2.3 at 4.6×10^{-4} eV to 1.5 at 0.005 eV. Nothing seems to suggest however from the EQM values that such a ratio could agree with Lee and Liu's results given the monotonically increasing behaviour with the energy in an apparent effort to match the statistical predictions. Similar disagreement was also found between

measurements for the $O(^1D)+HD$ reaction [36] and recent statistical results [37].

Bañares *et al.* [14] chose the inverse ratio (SH / SD) in their comparison with the experimental values of Lee and Liu. Whereas the QCT values remain constant over the energy range under consideration (between ~ 0.03 eV and 0.45 eV) suggesting an equal importance of both product arrangements, the predictions from a capture model shows a similar trend as our present results. Contrary to experiment, the formation of SD is favoured against the SH-forming channel and it is only when the energy increases up to ~ 0.35 eV that the situation becomes the opposite, something which is also suggested by both the SQM and MPPST results.

Figure 3: Ratio between ICS for the reactions $S(^1D) + HD \rightarrow SD+H$ and $S(^1D) + HD \rightarrow SH+D$ as a function of the energy (measured in eV). SQM results (black line) are compared with values calculated from the EQM (red line) and experiment (empty blue circles) reported in Ref. [8] and those reported by Lee and Liu [1] (black squares).

4. Conclusions

The $S(^1D)+HD$ reaction has been investigated by means of a statistical quantum method and phase space theory. Integral cross sections as a function of the collision energy have been calculated and compared, first at the low energy regime, with recent crossed molecular beam measurements and time independent exact quantum mechanical results. Extension of the energy range has enabled also the comparison with excitation functions from a previous experiment. Branching isotope effects are analyzed in terms of the collision energy.

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