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A three-dimensional quantum mechanical study of the F + H$_2$/D$_2$ reactions. On a new potential energy surface

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Abstract

We report quantum mechanical cross sections and rate constants for the title reactions, as calculated on the Stark–Werner potential energy surface. The calculations, carried out in the reagents arrangement channel by employing negative imaginary potentials, were done within the coupled-state approximation. The calculated cross sections were compared with quasi-classical trajectory calculations. The calculated rate constants for the two title reactions as well as their isotopic ratio were found to be in good agreement with experiment. Part of the study is devoted to showing the existence of strong tunneling processes caused by a thin potential barrier.

1. Introduction

This is our third publication dealing with quantum mechanical (QM) integral state-selected cross sections (CS) and rate constants (RC) for the following reactions:

$$F + H_2(v_i = 0, \ j_i) \rightarrow HF + H, \tag{I}$$

$$F + D_2(v_i = 0, j_i) \rightarrow DF + D. \tag{II}$$
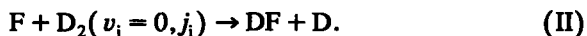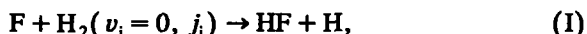
Whereas in the two previous articles [1,2] we reported results due to the T5A [3] potential energy surface (PES) and the 6SEC PES [4] respectively, here we present results for the Stark–Werner (SW) PES which has recently become available [5]. The SW PES is considered to be a better PES not only because it is based on more accurate ab initio calculations but also due to the facts (a) that a $J = 0$ calculation simulated correctly the electronic photodetachment spectrum of FH_2^- [6] and (b) that a

coupled-states treatment simulated correctly the vibrational state-to-state differential CSs for the reaction [7]

$$F + D_2(v_i = 0, \ j_i = 0) \rightarrow DF\left(v_f, \ \sum_{j_f} j_f\right) + D,$$
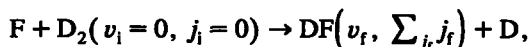
$$v_f = 0,1,...,4. \tag{1}$$

The abovementioned studies, in addition to many others [8–27] have aimed at probing the available PESs in order to learn to what extent they are capable of reproducing measured magnitudes, in general, and RCs, in particular. So far the T5A was found to yield, for the F + H$_2$ system [1], RCs which were smaller by about 50% than the experimental RCs. The situation was significantly improved with the introduction of the 6SEC. Here we calculated RCs for both the F + H$_2$ and F + D$_2$ systems [2] and obtained a nice fit for the F + D$_2$ system and a reasonable one for the F + H$_2$ system. Still, in the

case of $F + H_2$ the calculated RCs were 20–40% too small. It is important to mention that the results of the quasi-classical trajectory (QCT) calculations were similar [8].

In this Letter we shall not only show our recently calculated CSs and RCs and analyze them to a certain extent, as we did in previous cases [1,2] but we shall go further than that. It turns out that the SW

$j_i = 0$ CSs behave, around the threshold, in a peculiar way leading us to believe that we were encountering a new situation that could have an important impact on future studies. This subject is discussed below.

We shall not detail on the theory that led to our calculations but shall only say that the Schrödinger equation is solved in the reagents arrangement fol-
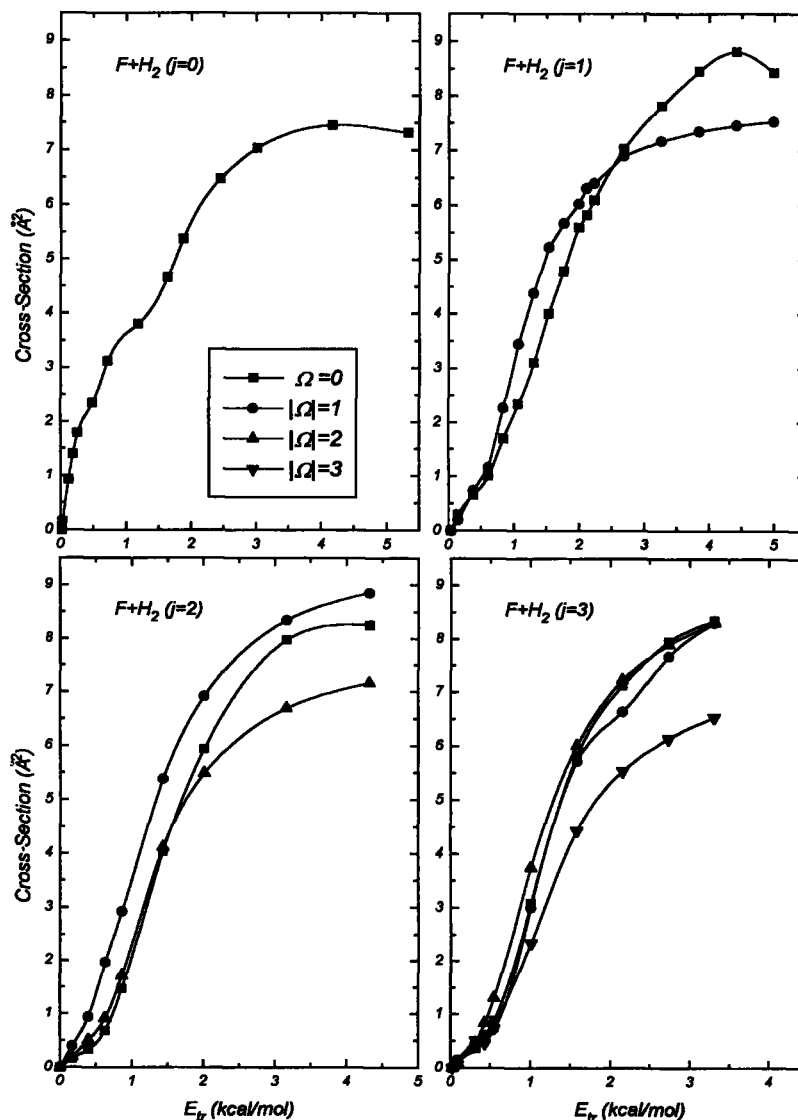

Fig. 1. Polarized ($|\Omega|$-dependent) cross sections as a function of translational energy for the reactions $F + H_2(v = 0, j, |\Omega|) \rightarrow HF + H$; $j = 0, \ldots, 3$; $|\Omega| = 0, \ldots, 3$.

lowing the incorporation of negative imaginary potentials (NIPs) [28–34]. As a result, for a given J (the total angular momentum quantum number) and Ω (its z-component in the body-fixed system) we calculate the inelastic (elastic) probabilities $P(v_f j_f \leftarrow v_i j_i| J\Omega)$. Consequently, the corresponding initial

state-selected reactive probabilities for a given J and Ω are obtained from the expression

$$P_r(v_i j_i| J\Omega) = 1 - \sum_{v_f j_f} \sum_{\geq |\Omega|} P(v_f j_f \leftarrow v_i j_i| J\Omega).$$
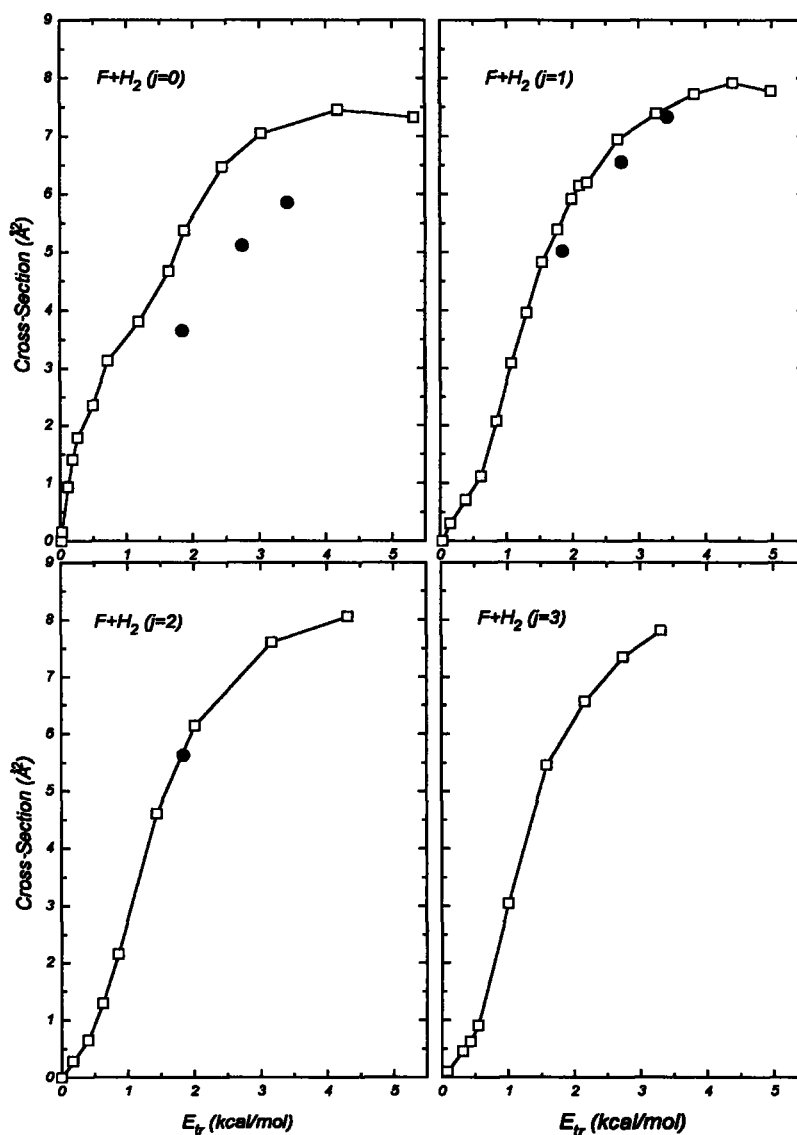
(2)

Fig. 2. Cross sections as a function of translational energy E_{tr} for the processes $F + H_2(v = 0, j) \rightarrow HF + H$; $j = 0, \ldots, 3$. □ Quantum mechanical (coupled-states) cross sections (present), ● quasi-classical cross sections (Ref. [9]).

It is important to mention that the numerical treatment is carried out within the coupled-states approximation [35] but it is equally important to emphasize that this approximation was found to be exceptionally accurate and reliable for the two title reactions [1,2,7].

2. Results

2.1. Cross sections

To calculate an integral CS one must first obtain the polarized, i.e. Ω-dependent, CS. Since these are important magnitudes per se, we shall present them as well.

2.1.1. Polarized (Ω-dependent) cross sections

Once the reactive (J, Ω) probabilities are given (see Eq. (2)), the corresponding (state-selected) CSs are calculated from the equation

$$\sigma(v_i j_i \mid \Omega) = \frac{\pi}{k_{v_i j_i}^2 (2j_i + 1)} \sum_{J \geqslant |\Omega|} (2J + 1)$$

$$\times P_r(v_i j_i \mid J\Omega), \tag{3}$$

where $k_{v_i j_i}$ is the corresponding wave number.

Polarized CSs for reaction (I) are presented in Fig. 1 for $j_i = 0, 1, 2, 3$ (similar results were obtained for $F + D_2$). It can be seen from these results that (a) the $\Omega \neq 0$ CSs cannot be considered negligible compared to the $\Omega = 0$ CSs, not even at the threshold region and (b) neither can they be assumed to be similar to the $\Omega = 0$ CSs. These remarks are important in view of the tendency, in many approximate QM treatments to avoid calculating the Ω-dependent CSs and employing one of the above (contradictory) assumptions.

Recalling the results for the T5A [1] PES it is noticed that here, in contrast to the T5A case, the dependence on Ω is much weaker. For instance, in the case of T5A not only were the $\Omega = 0$ CSs dominant but the $|\Omega| = j_i$ CSs were found to be smaller by 50% or less. With the SW PES, however, the differences are not larger than 20%. This is most probably due to the fact that the SW PES has a much wider cone of acceptance than the T5A. It is interest-

ing to mention that a similar study for the 6SEC places, in this respect, the 6SEC as an intermediate case.

2.1.2. Integral state-selected cross sections

Integral state-selected QM CSs for reactions (I) and (II) are presented in Figs. 2 and 3 respectively. In addition to the QM results we show a few QCT CSs [9]. In the case of $F + H_2$ it was only for $j_i = 0$ that we found large discrepancies between the two types of results. Small deviations were still noticeable for $j_i = 1$ but seemed to disappear altogether once $j_i \geqslant 2$. The case for $F + D_2$ differed somewhat: here even for $j_i = 0$ the discrepancies between the two types of CSs were small. It could be of interest to mention that essentially the same situation was encountered in our previous 6SEC PES study.

The energy-dependent CSs for both reactions and for $j_i \leqslant 1$ are seen to increase from $E_{tr} = 0$ (namely, without threshold), indicating a situation of no potential barrier. In this sense the present results differ significantly from the 6SEC ones where a clear threshold was encountered. Consequently, the question is: does the SW PES possess a barrierless (vib-rotational) *adiabatic* potential or could there be a different reason namely some kind of a quantum effect. We shall refer to this question in Section 3.

2.2. Rate constants

The cross sections presented in Figs. 2 and 3 were used to calculate rate constants k_{F+H_2} and k_{F+D_2}, taking into account the thermal distributions of collision energies and rotational states and including the multiple surface coefficient as was done in earlier studies [7]. The rate constants are presented in Table 1 and in Figs. 4a and 4b where they are compared with the results of QM calculations for the 6SEC PES and with experiment.

In general, the agreement between the QM RCs and experiment is satisfactory for the two surfaces. For $F + H_2$, for both PESs the QM RCs are close to the experimental ones at high temperatures and deviate from them to some extent as the temperature is lowered, becoming somewhat higher than the experimental values for the SW PES. The activation energy for the SW PES is lower than the average experi-

mental value by about 0.35 kcal/mol, while for the 6SEC PES it is higher than the experimental value by about 0.2 kcal/mol. For $F + D_2$, again agreement with experiment is good at high temperatures for both PESs. For the SW PES the RCs become somewhat higher than the experimental values at low temperatures, while for the 6SEC PES the agreement

continues to be good over the whole temperature range. The activation energy for the SW PES is lower than the average experimental value by about 0.25 kcal/mol, while for the 6SEC PES it is approximately equal to the experimental value.

QM kinetic isotope effects k_{F+H_2}/k_{F+D_2} for the SW and 6SEC PESs are presented in Fig. 4c where
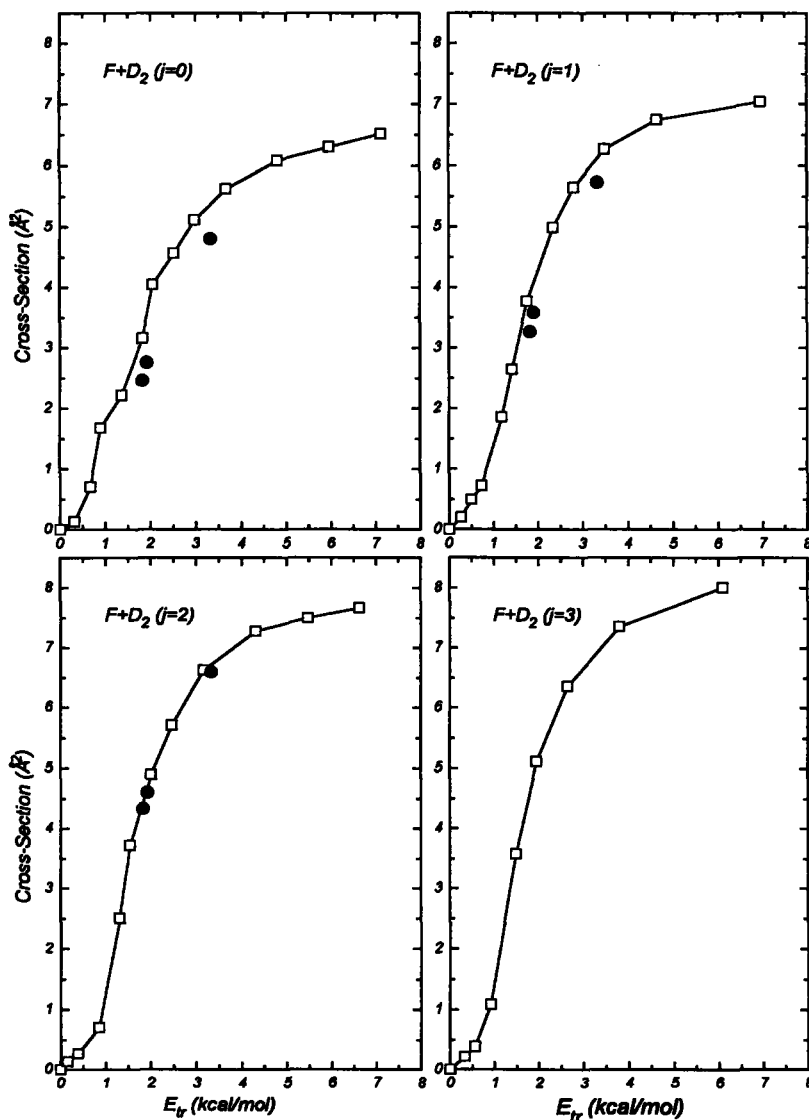

Fig. 3. Cross sections as a function of translational energy E_{tr} for the processes $F + D_2(v = 0, j) \rightarrow DF + D$; $j = 0, \ldots, 3$. □ Quantum mechanical (coupled-states) cross sections (present), ● quasi-classical cross sections (Ref. [9]).

they are compared with the experimental values determined directly by Persky [10]. As can be seen, the results for the SW PES agree well with experiment, while the results for the 6SEC PES deviate significantly from the experimental values.

Another test for theory would be the comparison of the calculated intramolecular kinetic isotope effect k_{F+HD}/k_{F+DH}, for the F + HD reaction, with experiment [10]. So far no QM RCs for this system have been calculated for any PES. QCT calculations done
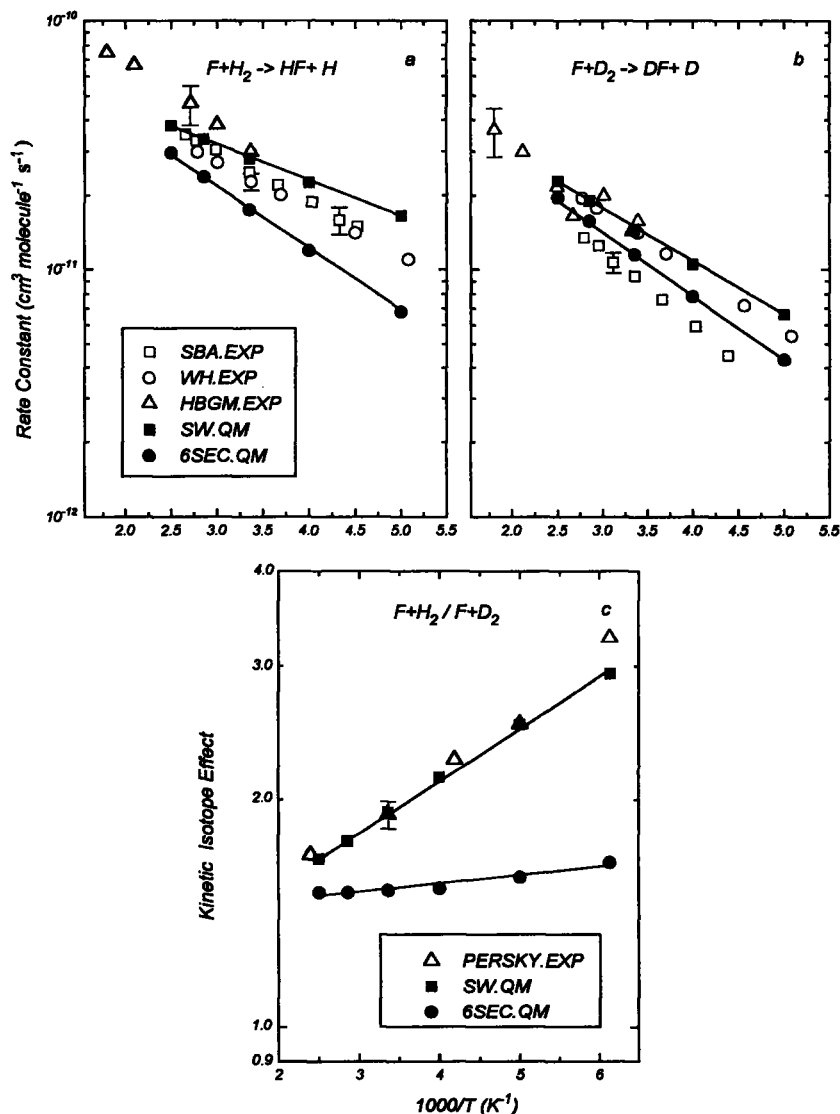

Fig. 4. Rate constants as a function of $1000/T$ for the process $F + X_2(v = 0) \rightarrow XF + X$; X = H,D. (a) X = H; (b) X = D. ■ SW quantum mechanical (coupled-states) rate constants, ● 6SEC quantum mechanical (coupled-states) rate constants (Ref. [2]), ○ experimental rate constants (Ref. [14]), △ experimental rate constants (Ref. [15]), □ experimental rate constants (Ref. [16]). (c) Isotopic ratios k_{F+H_2}/k_{F+D_2} as a function of $1000/T$. ● 6SEC quantum mechanical (coupled-states) ratio, ■ SW quantum mechanical (coupled-states) ratio, △ experimental ratio (Ref. [10]).

for this system employing the 6SEC PES [8] show that this isotope effect is in good agreement with experiment. A comparable good agreement is also expected from a QM calculation, as it was shown [2] that QM effects are not significant for this surface and the QM rate constants k_{F+H_2} and k_{F+D_2} were only slightly larger than the QCT ones.

3. Analysis and discussion

This is the third time that we have calculated CSs and RCs for the title reactions. In each case a different PES was used but it is in this case that we think that the PES (namely the SW PES) behaves differently not only from the two previous PESs but also from PESs applied for other reactions. Therefore, we decided to devote a part of our present analysis to uncover this "mystery". To this end we calculated, for the 6SEC and the SW PESs, the
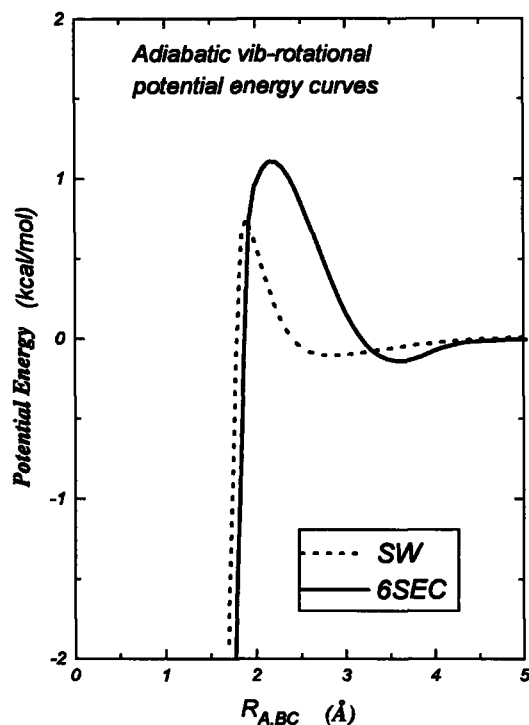

Fig. 5. Adiabatic potential energy curve along the entrance channel as calculated from Eq. (4). (– – –) SW potential energy curve, (———) 6SEC potential energy curve,

lowest adiabatic vib-rotational, R-dependent, potential energy curve $V(R)$ along the entrance (reagents) arrangement channel, namely:

$$V(R) = \langle \xi_{v=0, j=0} | U(R, r, \gamma) | \xi_{v=0, j=0} \rangle, \qquad (4)$$

Here, $U(R, r, \gamma)$ is the full PES and $\xi_{vj}(r, \gamma \,|\, R)$, for $v = 0$ and $j = 0$, is the lowest adiabatic vib-rotational $F + H_2$ basis function as calculated at a given value of R. In Fig. 5 are shown the SW and the 6SEC potential curves. It can be seen that the SW curve is not only lower than the 6SEC one but also much thinner. In Ref. [2] are presented the energy-dependent 6SEC CSs and they were found to exhibit a clear threshold which is expected from the shape of the 6SEC potential barrier shown in Fig. 5. However, the SW CSs do not exhibit any threshold behavior neither for $F + H_2$ nor even for $F + D_2$. But as can be seen this is not due to a missing potential barrier but because the barrier is thin enough to permit significant tunneling.

Table 1
Theoretical and experimental rate constants for the reactions $F + H_2$, $F + D_2$ [a]

$T(K)$	Experiment [b]			QM	
	WH [c]	SBA [d]	HBGM [e]	SW	6SEC
(a) $F + H_2 \rightarrow HF + H$					
200	1.14	–	–	1.66	0.68
250	1.76	1.83	–	2.25	1.19
298	2.33	2.48	2.91	2.81	1.75
350	2.89	3.14	3.92	3.35	2.37
400	–	–	4.85	3.80	2.97
A [a]	10.0	12.0	21.6	8.6	12.9
E_a [f]	0.86	0.93	1.18	0.66	1.17
(b) $F + D_2 \rightarrow DF + D$					
200	0.57	–	–	0.66	0.43
250	0.99	0.61	–	1.05	0.78
298	1.41	0.95	1.39	1.46	1.15
350	1.86	1.33	1.88	1.90	1.57
400	–	–	2.34	2.28	1.96
A [a]	9.1	9.3	10.6	7.8	8.8
E_a [f]	1.10	1.35	1.20	0.97	1.20

[a] Units of 10^{-11} cm^3 molecule^{-1} s^{-1}.
[b] Values were calculated from the reported Arrhenius fits to the experimental data.
[c] Wurzberg and Houston [14].
[d] Stevens et al. [16].
[e] Heidner et al. [15].
[f] Units of kcal/mol.

In Ref. [2] we speculated that only a significant QM effect could "push" the theoretical $F + H_2$ RCs into the experimental range. For this sake we suggested the existence of a (van der Waals) potential well located just in front of the potential barrier in the entrance valley. As is noticed the SW PES creates such a QM *push*, however, by possessing a barrier instead of a potential well. This barrier is solid enough to create a classical threshold but then, thin enough, to allow transitions due to tunneling.

It is important to remember that this treatment, like all our previous QM calculations, was carried out employing one single PES. There are good reasons to believe that more than one PES takes part in the reactive process [36] and if this is the case then part of the reported results and even some of the conclusions could be affected.

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