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Cross Sections and Rate Constants for the $F + X_2(v=0, j) \rightarrow XF + X$ ($X = H, D$) Reactions: A Three-Dimensional Quantum Mechanical Calculation[†]

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In this letter we report on quantum mechanical cross sections and rate constants for the title reactions as calculated on the 6SEC potential energy surface. The calculations, carried out in the reagents arrangement channel employing negative imaginary potentials, were done within the coupled-state approximation. The calculated cross sections were compared with quasi-classical trajectory calculations and in the case of $F + H_2$ also with (the four available) formally accurate quantum mechanical ones. The most pronounced quantum effects were found in reactions with the diatom reagent in the $j = 0$ level. However, these effects were not large enough to cause a significant increase in the rate constants as compared to those calculated by the QCT method even at very low temperatures. As for the $F + D_2$ reaction, the good agreement that was found earlier between quasi-classical rate constants and experiment was kept in the current QM calculations.

The $F + H_2$ system is one of the most important systems in few-atom chemical dynamics and numerous experimental and theoretical studies have been devoted to investigate it.^{1–33} Despite the enormous effort invested and the impressive progress made over the years, none of the theoretical studies were able to reproduce all the experimental results (see refs 25 and 32). This failure can be mainly attributed to errors in the potential energy surfaces (PES) available to date.

Several potential energy surfaces (PES), some of them based on ab initio calculations, have been proposed and applied in quasi-classical trajectory (QCT) and quantum mechanical (QM) calculations. Among them are the M5 PES proposed by Muckerman¹⁶ more than 20 years ago, the extended LEPS²¹ surface developed by Takayanagi and Sato, the T5A,^{20a} 5SEC,^{20b} and 6SEC^{20c} developed by Truhlar and co-workers and the surface developed recently by Stark and Werner, named SW.³⁴ A few of these surfaces were used for calculations of rate constants, with various degrees of success to reproduce the reported experimental results. Among the most recent attempts are the QCT calculations of Rosenman and Persky,³² who found that for the T5A surface the rate-constants for $F + H_2$ were more than 50% smaller than the experimental measurements. The deviations for $F + D_2$ were smaller but still very significant. A similar calculation using the 6SEC surface yielded an improved fit. For $F + H_2$ the calculated rate constants came closer to the experimental ones, although they were still significantly different at the low-temperature region (around 200 K). For $F + D_2$ the agreement with experiment was found to be very good. It was suggested³² that the 6SEC surface may give an even better agreement with experiment, if quantum mechanical effects are included in the calculations. Quantum effects, like tunneling, are expected to increase the reactivity for $F + H_2$ more than for $F + D_2$ and to have its greatest influence at low temperatures, where the discrepancy between the measured and calculated rate constants were most pronounced. In the present study we examine this prediction via the coupled-state method.

Our approach, has three basic components.³⁵

(a) Application of the perturbative type Schroedinger equation (SE) to treat nonreactive collisions taking place in a given arrangement channel (AC):³⁵

$$(E - H)\chi_{t_0} = V_{t_0}\psi_{t_0} \quad (1)$$

Here E is the total energy, H is the hamiltonian, χ_{t_0} is the short-range part of the total wave function ψ_{t_0} , ψ_{t_0} is its unperturbed part representing essentially the asymptotic incoming component of ψ_{t_0} (thus, $\psi_{t_0} = \chi_{t_0} + \psi_{t_0}$), V_{t_0} is a t_0 -dependent perturbation, and t_0 (and t) stands for the set of relevant quantum numbers.

(b) Conversion of eq 1, which treats nonreactive processes, into an equation that treats reactive processes. This is achieved by adding to the hamiltonian H in eq 1 in an ad hoc way, a negative imaginary potential (NIP)³⁷ in such a manner as to decouple the reactive ACs.

(c) Conversion of the scattering problem into a bound-type system by introducing one additional NIP in the asymptotic region, thus permitting the expansion of χ_{t_0} in terms of L^2 basis sets.^{35,36}

The aim of the calculation is to obtain the following (nonreactive) S-matrix elements:

$$S(r \leftarrow t_0) = \left(\delta_{rt_0} + \frac{m}{i\hbar^2} \langle \psi_r | V_t | (\chi_{t_0} + \psi_{t_0}) \rangle \right) \exp(i\varphi_t) \quad (2)$$

where δ_{rt_0} is the Kronecker delta function and φ_t is the n th (elastic) phase shift related to ψ_t . These matrix elements, once derived as a function of various initial conditions, are used to calculate the reactive state selected total cross sections (CS) according to the following formula:

$$\sigma(n_j j_0) = \frac{\pi}{k^2(n_j j_0)(2j_0 + 1)} \sum_{|\Omega| \leq j_0} \sum_{J \geq |\Omega|} (2J + 1) \{ 1 - \sum_n \sum_{j \geq |\Omega|} |S(nj \leftarrow n_j j_0 | J \Omega)|^2 \} \quad (3)$$

where n (n_0) and j (j_0) are vibrational and rotational quantum numbers, J and Ω are the total angular momentum and its z component, $k(n_j j_0)$ is the initial wave vector and $S(nj \leftarrow n_j j_0 | J \Omega)$ stands for $S(r \leftarrow t_0)$.

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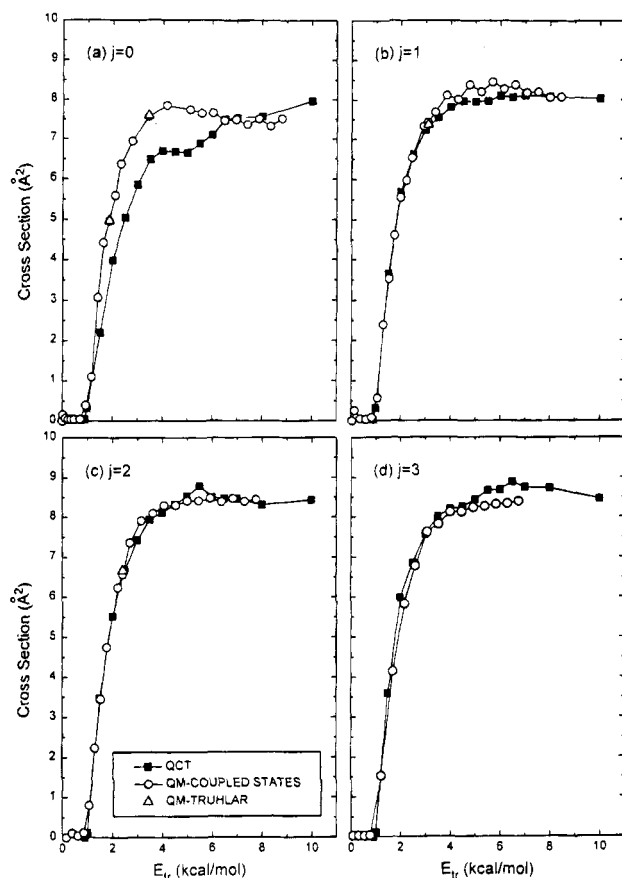


Figure 1. Cross sections as a function of translational energy E_{tr} for the processes: $F + H_2(\nu=0, j) \rightarrow HF + H$. (a) $j = 0$; (b) $j = 1$; (c) $j = 2$; (d) $j = 3$. (○) Quantum mechanical (coupled states) cross sections (present results), (△) quantum mechanical (exact) cross sections,²⁶ (■) quasi-classical cross sections.³²

The advantage of performing the calculations only in the reagents AC becomes apparent when approximate treatments are applied. The various approximations will yield reliable results for nonreactive systems, namely, single AC systems, but they become much less reliable when applied to cases that require treating more than one AC. In the present study, we applied the coupled states approximation.^{39–41} That approximation was found in many (nonreactive) studies to yield reliable results even for some of the most detailed magnitudes, such as state-to-state differential CSs. We applied this approximation in our recent study of the $F + H_2$ reaction performed on the T5A PES and compared the energy-dependent CSs, as calculated for two different initial rotational states, i.e., $j = 0, 1$ with exact CSs.³³ For all practical purposes the two types of results, along the whole considered energy range, were identical.

Details regarding the numerical parameters employed in the present calculation are described in ref 33. However, for completeness, we refer to one parameter, namely, the upper bound of the translational interval R_{as} which caused some difficulties. In the case of the T5A PES well-converged results were obtained for $R_{as} = 4A$. In case of the 6SEC PES due to a (spurious?) shallow potential well located at $R \sim 4A$ we had to shift R_{as} to 6A before convergence could be attained.

In Figure 1 are presented the state-selected total CSs as a function of translational energy, calculated for different initial rotational states, namely, $j = 0–3$, for the $F + H_2$ reaction. In addition to the coupled states results, we also present QCT cross sections³² and few formally accurate QM results.²⁶ With respect to the comparison with the accurate results, it is seen that the two QM treatments yield identical results, not only for $H_2(j=0)$

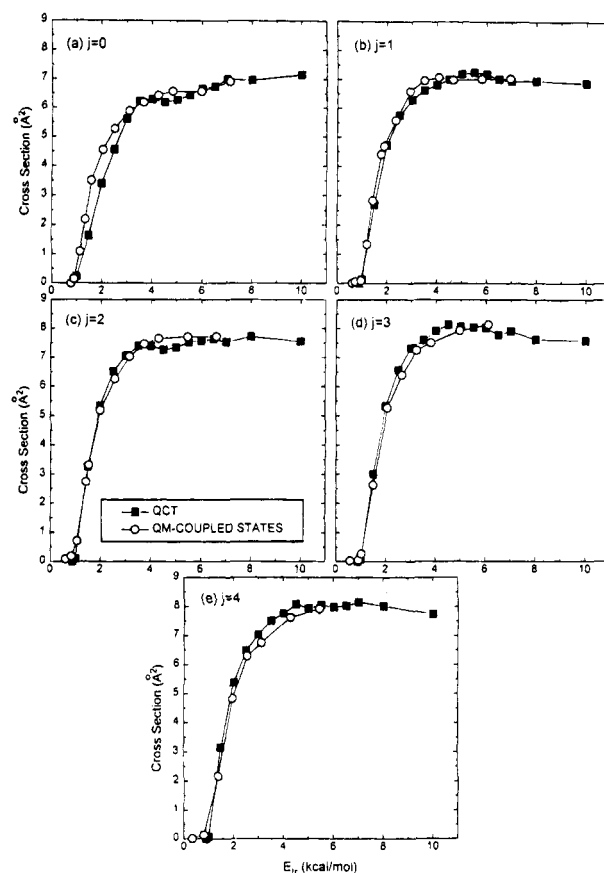


Figure 2. Cross sections as a function of translational energy E_{tr} for the processes: $F + D_2(\nu=0, j) \rightarrow DF + D$. (a) $j = 0$; (b) $j = 1$; (c) $j = 2$; (d) $j = 3$; (e) $j = 4$. (○) Quantum mechanical (coupled states) cross sections (present results), (■) quasi-classical cross sections.³²

but also for $H_2(j=1)$ and $H_2(j=2)$, where calculations involving $\Omega \leq 2$ were needed. As for the comparison with QCT results the following can be said: Along the range of collision energies from 1.5 to 6.5 kcal/mol the QM $j = 0$ CSs are significantly larger than the respective QCT ones. This is the most prominent quantum effect found here and it is lost when the rotational level of the H_2 reagent is excited. Along most of the energy range the QM $j \neq 0$ CSs overlap very nicely with the corresponding QCT ones. The main difference between the two types of results for $j \neq 0$ is seen in the threshold region, where tunneling processes enable QM reactivity to appear at collision energies beneath the classical barrier.

The cross section for the isotopic analogue $F + D_2$ as a function of collision energy is presented in Figure 2. For this reaction there are no other QM results and the current values are the first to be published. As we saw in the $F + H_2$ case, the most prominent quantum effects exist in the $j = 0$ reaction. Here, the difference between the QM and QCT curves seems to be smaller than for $F + H_2$, and it is probably due to the heavier mass of the D_2 which causes quantum phenomena to be less pronounced. However, although these quantum effects are relatively small, they appear at the range of collision energies which contributes most to thermal rate constants. Thus the ratio between QM and QCT rate constants for the two isotopic analogues ($F + H_2$, $F + D_2$) is about the same. As for reactions with $D_2(j=1–4)$, the agreement between the QM and QCT calculation is quite good. Here, in contrast to what was found for the $F + H_2$ reaction, there is less tunneling in the threshold region.

The cross sections presented in Figures 1 and 2 were used to calculate rate constants, taking into account the thermal distribu-

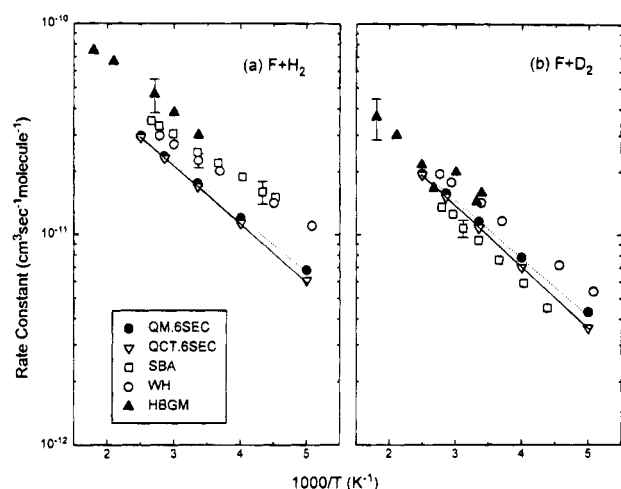


Figure 3. Rate constants as a function of $1000/T$ for the process: $F + X_2(v=0) \rightarrow XF + X$; $X = H, D$. (a) $X = H$; (b) $X = D$. (●) Quantum mechanical rate constants (present results), (▽) quasi-classical rate constants,³² (○) experimental rate constants,⁶ (▲) experimental rate constants,⁷ (□) experimental rate constants.⁸

TABLE 1: Calculated Rate Constants for the Reactions $F + H_2$ and $F + D_2$ ^a

T (K)	$F + H_2$		$F + D_2$	
	QM	QCT	QM	QCT
200	0.68	0.61	0.43	0.36
250	1.19	1.13	0.78	0.70
298	1.75	1.69	1.15	1.08
350	2.37	2.32	1.57	1.51
400	2.97	2.92	1.96	1.93

^a Units of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

tions of collision energies and of initial rotational states and using the same procedure as in the QCT calculations.³² Rate constants are presented in Table 1 and in Figure 3.

It was already shown³² that the 6SEC PES gives for $F + H_2$ QCT rate constants which approach the experimental results at high temperatures, but the discrepancy becomes larger as the temperature is lowered. The results reported here (Figure 3a) show that the QM and the QCT rate constants are not much different. It means that the discrepancy between the calculated rate constants and the measured ones is not caused by the QCT method but is probably due to the features of this PES. The small increase in the rate constants given by the current QM calculations is also observed for the $F + D_2$ reaction (Figure 3b).

The conclusions from this study are as follows:

(a) The QM and the QCT treatments yielded significantly different CSs only for $j = 0$. This applies to the two systems but they are more pronounced for the $F + H_2$ reaction. However, since the abundance of the $j = 0$ level is low (13% for H_2 and 18% for the D_2 at 300 K), these differences were not large enough to give significantly different rate constants in comparison to those given by the QCT method. The contribution of tunneling near threshold for the higher j values was also small and did not affect much the final results. Consequently, while the applied 6SEC PES is capable of reproducing the experimental rate constants for the $F + D_2$ system quite well along the whole studied temperature range, it is much less successful in reproducing them for $F + H_2$, in particular in the low-temperature region.

(b) The good agreement between the QCT and QM cross sections and rate-constants indicates that the much applied QCT method is a very effective and useful one for the $F + H_2$ system and probably for other simple systems.

(c) Although the 6SEC PES has a low barrier and a much wider "cone of reception" than the previous (the M5 and the T5A) PESs, it still predicts too low rate-constants for $F + H_2$, especially at low temperatures. Lowering the barrier will not solve the problem. It may improve the agreement for $F + H_2$, but at the same time may spoil the good agreement obtained for $F + D_2$. It could be that a similar PES, but with van der Waals shallow potential wells located in the quasi-asymptotic region, will give results in better agreement with experiment. Such potential wells may form conditions for Feshbach-type resonances and in this way enhance tunneling processes. These processes, which are expected to be much more pronounced for $F + H_2$ than for $F + D_2$, will enhance the reaction in the low-energy region and reduce the differences between the measured and calculated rate constants for $F + H_2$ but will not affect significantly the results for $F + D_2$.

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