# The effect of van der Waals resonances on reactive cross sections for the F + HD reaction

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## Abstract

In this Letter we present integral cross sections for the F + HD reaction on the well-studied Stark-Werner (SW) potential energy surface. Time-independent quantum reactive scattering calculations were carried out using very small energy intervals, that can resolve sharp van der Waals resonance structures. It has been found that the sharp van der Waals resonance features still survive in the calculated integral cross sections in the collision energy range of 1.3-2.3 kcal/mol even after total angular momentum averaging.

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## 1. Introduction

Dynamical resonance in chemical reactions has long attracted much attention from both experimental and theoretical points of view since the discovery of quantum-mechanical resonances in calculated reaction probabilities for three-dimensional atom-diatom reactions in the early 1970s [1,2]. It is now established that the F + HD → HF + D reaction is unique in that a quantum-mechanical resonance structure appears in the integral cross section even after impact parameter averaging. Sophisticated crossed molecular beam experiments of Liu and coworkers show a clear step-like feature in the measured integral cross section around the collision energy of 0.5-0.8 kcal/mol [2-5]. The quantum reactive scattering calculations on the accurate ab initio Stark-Werner (SW) potential energy surface [6] mostly reproduced this step-like feature although a deviation was found in the absolute magnitude of the resonance contribution [3,4]. Theoretical calculations [4,7] also revealed that the origin of this step-like feature is a consequence of the dynamics resonance state localized behind the reaction barrier at the collinear F—H—D configuration around the transition-state region. It was also confirmed that the resonance state corresponds to the temporal collinear molecule having vibrational quantum numbers (003).

Very recently, Liu and coworkers [2,3,8] have experimentally found the resonance fingerprint for the F + HD → HF + D reaction in a different collision energy region. They have observed a remarkable oscillatory forward-backward feature in the measured state-resolved differential cross section in the collision energy range of 1-3 kcal/mol. The quantum scattering simulation on the SW surface showed qualitative agreement with the experimental result; however, the relative magnitudes are not completely consistent. Thus, Liu and coworkers have concluded that further refinement of the F-H-H potential energy surface should be performed.

In this Letter, we will focus on the effect of van der Waals resonances whose wavefunctions are localized in the shallow potential well in the HF + D exit region on the integral cross section. Previous theoretical studies using the SW potential surface already

showed that the van der Waals resonances appear in the collision energy region of 1-4 kcal/mol [7, 9-11].   As the same time, it was found that these resonance peaks are quite sharp. A typical energy width is only 0.005 kcal/mol, which is much smaller than the standard molecular beam experimental condition.   Therefore, this suggests that these van der Waals resonances may be quite difficult to be observed experimentally.   As a result, the effect of the van der Waals resonances on the integral cross section did not attract much attention so far. In fact, the previous calculations of the integral cross sections for the F + HD reaction were performed with a relatively large energy grid $\delta E$ [4, 12-17].   For example, Skodje et al. [4] have done the calculations with $\delta E \sim 0.06$ kcal/mol.   A somewhat small energy grid ($\sim 0.028$ kcal/mol) was used in the theoretical study of Tzeng and Alexander [14].   More recently, Fazio et al. [16] have carried out quantum scattering calculations using a new potential energy surface (called PES III) with $\delta E$ being $\sim 0.1$ kcal/mol.   Notice that these numerical values are still larger than the typical width due to the van der Waals resonance state.   However, it should be emphasized that weak oscillating structures are clearly seen in the previously calculated integral cross sections in the collision energy range of 1-3 kcal/mol (see Fig. 4 in Ref. 14, for example).   Here we speculate that these weak features come from the D···HF van der Waals resonances.   Motivated by this consideration, in this Letter, we will investigate if the sharp van der Waals resonances still survive or not in the calculated integral cross sections on the SW potential energy surface even after angular momentum averaging.

## 2. Computational Method

We have employed a closed-coupled, time-independent quantum reactive scattering method on the SW potential energy surface [6].   The calculations were mostly carried out using the ABC code of Skouteris et al. [18] but a part of the calculations were performed with our own code [10] based on the adiabatically adjusting, principal axes hyperspherical (APH) approach developed by Pack and Parker [19].   Numerical parameters were carefully chosen

to obtain fully converged computational results. The maximum value of the projection quantum number ($\Omega_{max}$) of the total angular momentum $J$ was set to be 5. We have performed the scattering calculations up to $J = 22$.

In order to obtain detailed resonance structures in calculated reaction probabilities, we have first done the calculations in the total energy range of 5.373-7.769 kcal/mol with the energy interval being 0.023 kcal/mol. When we found the resonance fingerprint in the calculated probabilities, we have further reduced the energy interval into 0.001 ~ 0.002 kcal/mol depending on the nature of the resonance.

## 3. Results and discussion

Fig. 1 shows the reaction probabilities for the F + HD($v = j = 0$) $\rightarrow$ HF/DF + D/H reaction as a function of the collision energy for each total angular momentum quantum number $J$. Here $v$ and $j$ are vibrational and rotational quantum numbers of HD, respectively. In the case of $J = 0$, we can see two very sharp resonances at $E = 0.230$ and 0.743 kcal/mol, where $E$ is the collision energy. These two resonances have been previously assigned to the quasi-bound F$\cdots$HD($v = 0$, $j = 1$ and 2) van der Waals complexes, respectively [10, 20]. Less narrower resonances than these entrance van der Waals resonances seen at $E = 1.313$ kcal/mol and higher energies are associated with the quasi-bound complexes localized in the exit D + HF van der Waals region. For example, the most intense resonance peak at $E = 1.313$ kcal/mol can be assigned as the D$\cdots$HF($v = 3$, $j = 0$) complex and higher-energy resonances are associated with the rotationally excited states of HF. Since the F$\cdots$HD entrance channel resonances are extremely sharp, we focused only on the D$\cdots$HF exit channel resonances for $J > 0$. The most important point found from Fig. 1 is that the resonance width is quite small for all values of $J$ and that only the resonance position shifts toward higher energies as $J$ increases. Castillo and Manolopoulos [9] have previously obtained the rotational constant for the lowest D$\cdots$HF van der Waals resonance to be 0.133 meV by plotting the resonance

position as a function of $J(J+1)$. They have found that this value is close to the value of 0.126 meV that one would calculate for the linear equilibrium geometry of the D-HF van der Waals well on the SW potential energy surface. In addition, they have further carried out standard resonance stabilization calculations to confirm their assignment.

The integral cross sections for the F + HD($v = j = 0$) → HF/DF + D/H reaction obtained in this work are plotted in Fig. 2 as a function of the collision energy. Overall agreement with the results of Skodje et at. [4] is found to be excellent. However, it is clearly seen that the cross section for the F + HD → HF + D reaction has a significant oscillating structure in the collision energy range of 1.2-2.3 kcal/mol although its contribution in absolute magnitude is not very large. However, we can see about 10 % enhancement in reactivity at a resonance position, which cannot be, of course, ignored. As can be predicted, the resonance contribution to the cross section for the DF + H product channel is found to be quite small. This is quite reasonable since these resonances are associated with the HF-D van der Waals potential well not with the DF-H well.

It may not be appropriate to compare the computed differential cross sections at a given translational energy to the experimental one since there exists a finite collision energy width that is probably larger than the van der Waals resonance width, in usual molecular beam experiments. Thus, the comparison between theory and experiment should carefully be done by taking the effect of such experimental collision energy distribution into account.

We have shown that the very sharp van der Waals resonances significantly contributes to the total reactive cross sections. However, it should be emphasized that the positions and widths of such sharp resonances are, in general, strongly dependent of the topological feature of the potential energy surface employed. We have employed the SW potential energy surface throughout our calculations since this surface has been most extensively employed in previous quantum reactive scattering calculations [1]. In addition, it is quite well-known that the SW potential energy surface reasonably reproduces experimentally measured quantities at a qualitative level; however, it has been pointed out that further refinement is necessary for obtaining more quantitative agreement with the

experimental findings.  For example, we have previously pointed out that the SW surface has a unphysical exit barrier in the HF···D van der Waals region [21].  Skodje and coworkers [22] have recently shown that the modification of the van der Waals region of the SW surface significantly affects positions and intensities of the van der Waals resonances for the F + HD reaction.  Also, Aquilanti and coworkers [16,23-25] have developed a few versions of the F + $H_2$ potential energy surface that can describe the entrance and exit van der Waals regions more accurately.   In particular, it is well-known that the spin-orbit electronically nonadiabatic effect plays some roles in the F + $H_2$ entrance van der Waals region.   Finally, we would like to mention the most recent joint study of theory and experiment of Qui et al. [26] on the F + $H_2 \rightarrow$ HF + H reaction.   They have found dynamical resonances at a collision energy of 0.52 kcal/mol, that is attributed to both the ground and the first excited Feshbach resonances trapped in the transition state region and the HF($v$ = 3)-H van der Waals region. This experimental findings were well reproduced by the quantum reactive scattering calculations based on a new potential energy surface, that has been obtained from a new set of extensive ab initio electronic structure calculations [27].   Interestingly, this new potential energy surface has a deeper van der Waals well in the H + HF exit channel than the SW one. This suggests that the effect of the H-HF van der Waals is more important.   Presumably, this newly developed potential energy surface will definitely play a role in the future theoretical work.   We hope that the future quantum reactive scattering calculations for the F + $H_2$ reaction and its isotopic variants on this surface will employ a fine energy grid in order to fully resolve the sharp van der Waals resonances.


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**Figure Captions**

Fig. 1    Calculated total reaction probabilities for the F + HD( $v = j = 0$ ) $\rightarrow$ HF + D and DF + H reactions as a function of the relative translational energy.    The reaction probabilities are shown for each total angular momentum quantum number $J$.    Left and right panels show the results for F + HD $\rightarrow$ HF + D and F + HD $\rightarrow$ DF + H, respectively.

Fig. 2    Calculated integral reactive cross sections for the F + HD( $v = j = 0$ ) $\rightarrow$ HF/DF + D/H reaction as a function of the relative translational energy.    Expansion of the cross sections for the F + HD( $v = j = 0$ ) $\rightarrow$ HF/DF + D/H reaction in the energy range of 1.2-2.3 kcal/mol is shown in (b).
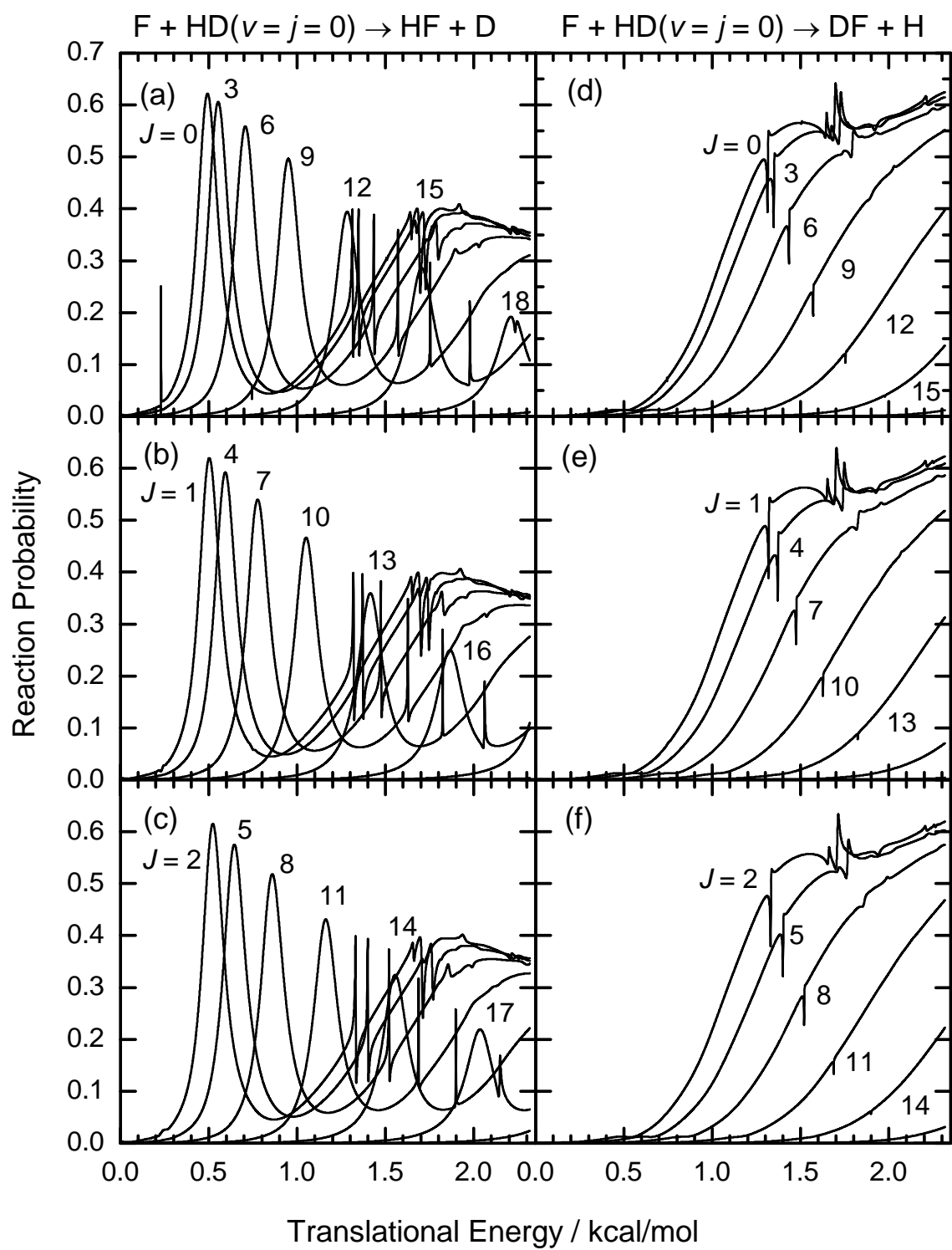
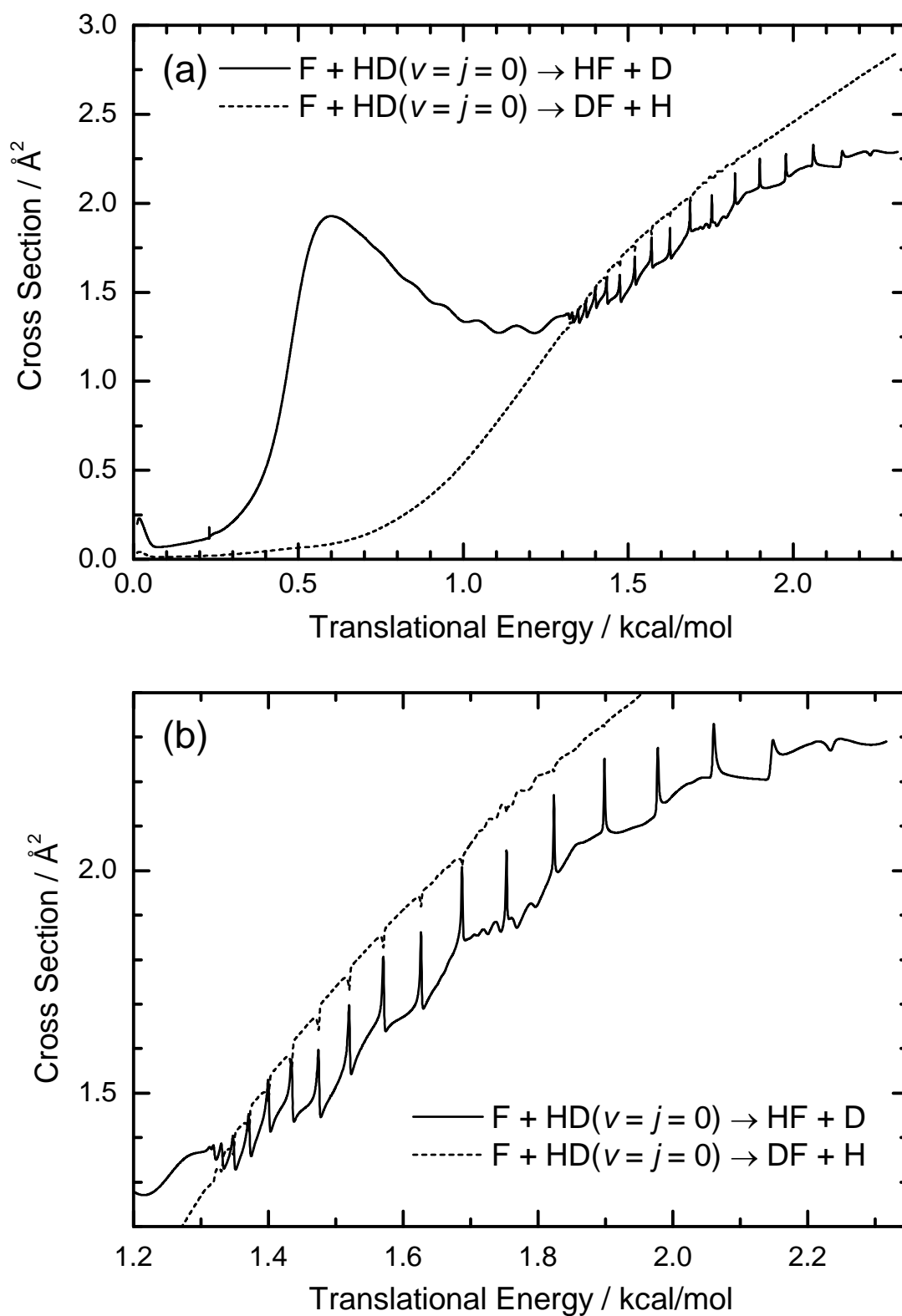F + HD($v = j = 0$) → HF + D          F + HD($v = j = 0$) → DF + H

Fig. 1

Fig. 2