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Citation: The Journal of Chemical Physics **113**, 3633 (2000); doi: 10.1063/1.1287840 View online: http://dx.doi.org/10.1063/1.1287840 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/113/9?ver=pdfcov Published by the AIP Publishing

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Reactive excitation functions for $F+p-H_2/n-H_2/D_2$ and the vibrational branching for F+HD

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(Received 13 March 2000; accepted 8 June 2000)

Complementary to our recent report on the F+HD reaction, the reactive excitation functions for the other isotopomers are presented. Through analysis of the differential cross section data, the collisional energy dependencies of product vibrational branchings for F+HD are also reported here. Several important conclusions can be drawn from this work. First, the transition-state properties, in particular the barrier height, of this reaction are well-characterized by the SW PES, despite its neglect of spin–orbit couplings. Second, contrary to the theoretical conclusion in recent literatures, an experimental observation is presented which seems to suggest that a resonance may indeed exist for the F+H₂ reaction in support of the original interpretation proposed by Lee and co-workers. Third, the vibrational branching for the F+HD→HF+D reaction elucidates another facet of resonance effects in the integral cross sections. Finally, the nonadiabatic reactivity of the spin–orbit excited F*(${}^2P_{1/2}$) atom is found to be small, which is in line with the conclusion inferred from a most recent, full quantum mechanical multisurface calculation. © 2000 American Institute of Physics. [S0021-9606(00)01233-2]

I. INTRODUCTION

The reaction of $F(^2P) + H_2$ and its isotopic variants have played a central role in the development of gas phase reaction dynamics.¹ These reactions have been extensively studied in a large variety of kinetic and dynamic experiments. A major breakthrough on the experimental front was the 1985 crossed-beam study of Lee and co-workers for F+H2/D2/ HD in the range of 0.7-3.4 kcal/mol collision energies.^{2,3} Anomalous forward scattering peaks in the vibrational stateresolved angular distribution were observed, which was attributed to quantum dynamical resonance phenomena. This experimental result has since then inspired numerous theoretical works both on the potential energy surface (PES) and on a series of quasi-classical trajectory (QCT) and quantum mechanical (QM) calculations of its reaction dynamics.⁴ Meanwhile, impressive experimental investigations of this reaction progressed. These include new crossed-beam experiments with improved resolution for $F+D_2$ in an extended collision energy range of 2–5.5 kcal/mol,^{5–7} a rotationally resolved differential cross section measurement for a few selected (v',j') states of HF in F+H₂ at $E_c = 3.64$ kcal/ mol,^{8,9} newer measurements of the rovibrational state distributions of HF from F+H₂ at 2.46 kcal/mol,¹⁰ and the rotational state distributions of HF(v'=3) over the energy range of 0.3-2.4 kcal/mol,11 and, most notably, the photodetachment spectroscopic approach of FH₂⁻ in direct probing the transition-state region of PES.¹²⁻¹⁴

The development of a highly accurate, state-of-the-art *ab initio* PES by Stark and Werner (SW)¹⁵ around the mid-90's has really made possible quantitative comparison between theory and experiments. Full QM calculations on the SW PES led to an unprecedented, nearly quantitative agreement with the photodetachment spectra.^{13,14} This confirms the *shape* of the transition state to be bent with a relatively flat

bending potential, but it cannot establish the reaction barrier height because of the uncertainty in the dissociation energy of the FH₂⁻ anion. On the other hand, using the SW PES, discrepancies between QM calculations and scattering experiments still persist for F+H₂,^{16,17} and particularly more so for $F+HD \rightarrow HF+D$.¹⁸ More significantly, the original interpretation of a resonant scattering mechanism proposed by Lee and co-workers in 1985 was challenged by a QCT investigation on the SW PES.19 The QM calculations and analysis performed later for F+H₂ seemed to confirm the alternative QCT line-of-center model that the sharp forward scattering of HF(v'=3) in $F+H_2$ is attributed to tunneling through the centrifugal barrier for large impact parameter collisions.4,16 Hence, at this point it appears that the experimental anomalies in angular distributions could be classical mechanics in origin.

There are other unsettled issues about this reaction. Since all experimental works performed so far involved an F-atom source with unknown spin-orbit contents (the spinorbit excited ${}^{2}P_{1/2}$ state lies 404 cm⁻¹ above the ${}^{2}P_{3/2}$ ground state), one of the long-standing questions is about their relative reactivities. Could the nonadiabatic reactivity of $F^*({}^2P_{1/2})$ account for the remaining discrepancies between theory and experiment? Facing this challenge, spinorbit effect has then been included in a refined version of the SW PES (hereafter HSW PES).²⁰ Its major effect was the increase of the barrier on the ground adiabatic $(1^{2}A')$ PES by 0.35 kcal/mol relative to its value on the spin-free SW PES. Paradoxically, QM simulations on the HSW PES (still single-surface calculations) for both $F+H_2$ (Refs. 20 and 21) and F+D₂ (Ref. 22) scattering experiments turned out to be somewhat worse than with the SW PES. Recently, the first "exact" QM multisurface scattering calculation, which includes all three HSW PESs, derivative coupling, spin-orbit

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FIG. 1. Excitation functions for the two isotopic channels of the F+HD reaction. The experimental results are shown with dots. The QM and QCT simulations on the SW PES are plotted with solid and dashed lines, respectively. The experiment is normalized to theory by a single scaling factor for both channels. (Adapted from Ref. 24.)

and Coriolis coupling effects, has been performed for the $F+H_2$ reaction.²³ It was found that for J=1/2 the reaction probability of $F^*({}^2P_{1/2})$ is less than 10% of that for $F({}^2P_{3/2})$. Although the reaction cross sections for $F({}^2P_{3/2})$ and $F^*({}^2P_{1/2})$ are yet to be calculated, it appears that the dominant feature of this reaction may very well be represented by the adiabatic dynamics on the lowest electronic PES, i.e., the SW PES.

Very recently, in a combined experimental and theoretical investigations of F+HD, we reported our experimental excitation function results.²⁴ Conclusive evidence was presented for the existence of a reactive resonance in the HF+D product channel. For illustrations and for ready comparisons with the other isotopic variants of this work, the results are replotted here in Fig. 1. As is seen, both QCT²⁵ and QM²⁴ calculations on SW PES gave excellent account for the total reactivity of the DF+H isotope channel. The agreement between QM and experiment is in fact nearly perfect, except for an experimental scaling factor. For the HF+D product channel, however, significant discrepancies by QCT are seen. Specifically, the peculiar steplike feature observed for $E_c < 1$ kcal/mol in experiment is entirely absent in the QCT result, and at higher energies QCT also underestimates its reactivity. By way of contrast, the QM calculation is in significantly better agreement with experiment. Both the posi-



FIG. 2. A schematic of the discharge F-atom beam source. The labels are (1), (2), and (4): Teflon or ceramic insulator; (3) and (5): S.S. electrodes; (6): skimmers. The O-rings are made of Kalrez 4079.

tion and the shape of the steplike feature at low energies are well reproduced, although the magnitude is off by a factor of 2. The reactivity at higher energies (>1 kcal/mol) also agrees well with experiment. As shown in Ref. 24, the peculiar steplike feature turns out to be an unmistakable fingerprint for resonance in the integral cross section of this reaction.

Since the "resonance hierarchy" is expected to follow the trend: $(F+HD\rightarrow HF+D)>(F+H_2)>(F+D_2)$ $>(F+HD\rightarrow DF+H)$, this new finding seems to reopen the original resonance interpretation,^{2,3} particularly for the $F+H_2$ reaction, of the landmark 1985 crossed-beam scattering experiments. This paper tries to shed some light on this issue by presenting the similar excitation function measurements for $F+p-H_2/n-H_2$ and D_2 . The collisional energy dependencies of the product vibrational branchings for F+HD are also included to further elucidate the resonance effect on integral cross sections, and to delineate the $F^*({}^2P_{1/2})$ contribution to total reactivity of this reaction. The latter is currently of considerable interests.^{4,10,11,20-23}

II. EXPERIMENT

The experiments were carried out in a crossed-beam apparatus.^{26,27} The experimental details, except the F-beam source, have been described previously,^{24,28} and thus will not be reiterated here. A schematic of the beam source is depicted in Fig. 2. Basically it is a modification of a standard piezoelectric transducer (PZT) pulsed valve. An extended housing is attached to a PZT pulsed valve to act as a gas holder so that the piezoelectric disk is not exposed to the corrosive gases. A pair of electrodes is mounted further downstream, and a dc high voltage, typically +1.1 kV, is applied to the front electrode. As the pulsed valve opens, the gas inside the extended channel (1 mm ϕ , 6 mm long) initiates the discharge and sustains it (i.e., a glow discharge) until the gas expands out of the channel. Also mounted between the two skimmers is a pair of deflection plates which

remove any discharge-generated ions from the beam. Typically, 5% F_2 in He or Ne (total pressure at 15 atm) was used in this work.

Two ways were used to characterize the mean speed of the F-atom beam. It was found that there is always a trace amount of discharge-generated H-atoms entrained in the beam. Assume that all supersonically expanded gases travel at the same speed. The Doppler-shift technique²⁹ was then employed to measure the beam speed through the (1+1)REMPI detection of the entrained H-atoms. Alternatively, one can monitor the (pulsed) discharge current. Knowing the distance from nozzle to the scattering center, the measurement of the time delay between the probe laser and the onset of the discharge current pulse also provided a convenient way to determine the beam speed. Agreement of these two methods is always within $\pm 3\%$. The collision energy determined in this fashion is confirmed to be accurate within 0.05 kcal/mol from the rotational state-resolved differential cross section measurements. It is known that discharge of F_2 can also generate a spin-orbit excited F* atom. Unfortunately, the relative amounts of $F({}^{2}P_{3/2})$ and $F^{*}({}^{2}P_{1/2})$ in the beam could not be measured with our setup. Hence, only a rough estimate can be made. (Since the assumption involved is not readily verified, one should not take this estimation too seriously. In the following only the F* contribution, not its relative cross section, will be reported.) The measured F beam speeds correspond to an effective source temperature of about 600 K for both seeded sources. Assuming the populations of the two spin-orbit states equilibrate at this temperature, this yields about 16% $F^*({}^2P_{1/2})$ present in our beam.

Before presenting the experimental results, we want to mention two more relevant points. First, the rotational temperatures of our target beams were estimated to be 150 K for H_2 (both *n*- H_2 and *p*- H_2), 100 K for D_2 , and 50 K for HD.²⁸ Accordingly, the theoretical results reported below, which are all based on the SW PES, have taken into account the initial *j*-dependencies of reaction cross sections whenever they are available. And the multisurface factor has been applied to all theoretical results in this work. Second, while the experimental excitation functions are not in absolute cross sections, they have all been normalized to one another. Hence, only a single scaling factor, which was based on the F+HD→DF+H reaction,²⁴ is involved in comparison with theory for all isotopomers.

III. RESULTS AND DISCUSSION

A. Excitation function for $F+n-D_2$

The excitation function for $F+D_2 \rightarrow DF+D$ is presented in Fig. 3. As is seen, both the threshold and the general shape are very much like that for $F+HD \rightarrow DF+H$ (Fig. 1), which suggests that the $F+D_2$ reaction is also dominated by direct scattering. Also shown in the figure are the QM^{22,30} and QCT³¹ results and the adiabatic barrier height of the SW PES. Small tunneling at low energy is discernible. The theoretical predictions, both QM and QCT, are in reasonable agreement with experiment. In particular, the experimental



FIG. 3. Excitation function for the $F+D_2 \rightarrow DF+D$ reaction (the upper panel). Both the QM (Ref. 22) and QCT (Ref. 31) results are based on the SW PES. The same scaling factor as F+HD is used here. The open circles are the experimental data points from Ref. 5. The low panel compares the isotope effects. The experimental result for $n-H_2$ is taken from Fig. 4, and the theoretical curve (the solid line) is the corresponding QM result.

scaling factor used here is the same as that for the $F+HD\rightarrow DF+H$ reaction; thus the agreement in magnitudes is quite significant.

The only previously reported experimental excitation function for this reaction is that by Faubel *et al.*⁵ Their results are depicted in Fig. 3 as the open circles for comparison. The scaling of their data is somewhat arbitrary by matching the three higher energy points. Their lower energy data clearly appear to be too low compared to either the theory or the present result.

B. Excitation functions for $F+n-H_2/p-H_2$

Figure 4 shows the excitation functions for the reactions of $F+n-H_2/p-H_2$. The purity of $p-H_2$ was greater than 98%, as reported previously.³² As expected, tunneling becomes more pronounced, in particular for the p-H₂ case. Even at energy as low as 0.2 kcal/mol, the reactive cross section is still quite significant. Again, both the magnitude and the global shape are reproduced reasonably well by a QM coupled-state calculation.³³ Similar to the comparison shown in Fig. 1 for $F+HD \rightarrow HF+D$, the QM calculation appears to overestimate the reactivity of $F+p-H_2$ at low energies (<0.5 kcal/mol). Another way to make a comparison between experiment and theory is to examine the ratio for different target molecules, as displayed in the lower panel of Fig. 3 for $\sigma_{\rm D_2}/\sigma_{\rm H_2}$ and of Fig. 4 for $\sigma_{n-{\rm H_2}}/\sigma_{p-{\rm H_2}}$. In this way, no scaling factor is involved; thus the experimental absolute ratio is compared directly with the theoretical value. Very good agreements can be seen in both cases. Based on the comparisons shown in Figs. 1, 3, and 4, we conclude that the main properties of the transition state including the bar-



FIG. 4. Excitation functions (the upper panel) for the $F+p-H_2$ (\bullet) and $F+n-H_2$ (\bigcirc) reactions. The QM coupled-state results are taken from Ref. 33, and the QCT simulation (for $p-H_2$ only) is from Ref. 31. The experimental scaling factor is the same as F+HD (Fig. 1) and $F+D_2$ (Fig. 3). The lower panel compares the initial *j*-dependencies. The solid line is the QM result.

rier height are well characterized by the SW PES, despite its neglect of spin–orbit effects. (The inclusion of spin–orbit effects will increase the barrier height spoiling the remarkable agreements with experiments.) This conclusion corroborates with recent QM simulations of the other reaction attributes using the HSW PES,^{20–22} as alluded to early.

A closer inspection of the experimental data also reveals a subtle, yet significant dependence of reactivity on the initial *j*-state of H_2 . At high collision energies, the rotation of H₂ apparently has a positive, abeit small, impact on its reactivity. Similar propensity has previously been observed for Cl+H₂ (Ref. 32). Both QM³³ and QCT³¹ (only p-H₂ is shown here for clarity) calculations display a similar trend. Its physical origin is purely classical, and can be traced to the long-range anisotropic interactions in the entrance valley. This stereodynamics also manifests itself in the intramolecular isotope branching ratio, as discussed previously for the F+HD^{24,25} and the Cl+HD reactions.³⁴ At lower energies $(E_c < 1.4 \text{ kcal/mol})$ such a *j*-dependency persists in the QCT calculation (not shown; see Ref. 31 for the *j*-dependencies), which is in sharp contrast with experimental observation. On the other hand, QM coupled-state calculations for $n-H_2$ and $p-H_2$ show the same propensity as experiment. Clearly, something quantum in nature, and probably more than just tunneling, must come into play at low energies. We conjecture that it is reminiscent of the very same resonance state as what we have recently found for the $F+HD\rightarrow HF+D$ reaction.24

The reason is the following. As shown previously,²⁴ the resonance state we identified for the F+HD reaction corresponds to "peak A" in its cumulative reaction probability.¹⁸ A similar feature (also labeled "peak A") is also present in

the F+H₂ reaction probability.¹⁶ There is, however, a significant difference between the two reactions. For the $F+HD \rightarrow HF+D$ reaction, at the resonance energy (i.e., "peak A") there is little or no direct reactive scattering. Thus it is an isolated resonance, which appears to survive the partial-wave averaging and manifests itself as a distinctive steplike feature in the integral cross sections (Fig. 1).²⁴ In the case of $F+H_2$, the QM calculation¹⁶ indicated that the onset for direct scattering shifts significantly closer toward its "peak A." Consequently, we expect a substantial contribution to the integral cross section from direct scattering even near the reaction threshold, which then blurs the resonance signature (i.e., the steplike feature) in the integral cross sections. Nevertheless, QM calculations also indicated that the "peak A" intensities for both reactions diminish with even one quantum of rotational angular momentum in either H₂ (Ref. 16) or HD²⁴ reactant. In other words, the resonance contribution, if it exists, should be more pronounced for p-H₂ than for n-H₂. The significant enhancement of reactive cross section observed at low energies for $p-H_2$ than for $n-H_2$ (Fig. 4) is entirely consistent with the resonance scenario in F+H₂. Furthermore, the opposite rotational dependencies predicted by QM and QCT at low energies can also be reconciled by the existence of a resonance state in this reaction provided that the absorbing potential used in Ref. 33 was sufficiently far out without missing the resonance contribution. A QM wave packet analysis for F+H₂, similar to that reported for F+HD,²⁴ has recently been performed, which firmly establishes the existence of a reactive resonance on the SW surface.³⁵ Thus, it seems that the theoretical balance is now tilt back in favor of the existence of a resonance for the F+H₂ reaction, though the correct interpretation of the landmark 1985 scattering experiment which was at higher collision energies could still remain an open question. In this regard, it is interesting to note that using semiclassical Regge pole analysis, with the help of Pade approximation, of the "exact" QM differential cross section for $F+H_2$, Sokolovski and Castillo³⁶ very recently argued that the anomalous state-selective forward scattering has a major resonance contribution.

C. Vibrational branching for F+HD

1. $F+HD \rightarrow HF(v')+D$

As depicted in Fig. 1 and discussed in details elsewhere,²⁴ the distinct steplike feature for $F+HD \rightarrow HF+D$ is indeed an imprint of the long-searched reactive resonance in the integral cross sections. The resonance fingerprint in product angular distribution has also been uncovered.³⁷ An interesting question then arises: is there any other experimental observable which signifies the existence of a resonance? and in what way? Presented here is the product vibrational branching.

We used the Doppler-selected TOF approach to measure the differential cross sections for F+HD. The experimental details have been given previously²⁷ and the resulted stateto-state differential cross sections for F+HD will be reported in the future. Here it suffices to say that once the product velocity-flux contour map is obtained, the integration of all



FIG. 5. A few examples of the product translational energy distributions for the F+HD→HF+D reaction. Also marked in the figure are the energetic onsets for the formation of HF(v') products from F(${}^{2}P_{3/2}$) and F*(${}^{2}P_{1/2}$). These P(E_t) distributions have been normalized to the excitation function (Fig. 1). Note the different scale for each collision energy, E_c in kcal/mol.

angles yields the desired product translational energy distribution $P(E_t) = d\sigma/dE_t$. A few of them for the HF(v') + D isotope channel are shown in Fig. 5 for illustration. The energetic onsets for different product vibrational states are also marked on the top. Quite obviously, the vibrational structures are well-resolved. Even after the integration of all angles (note: the energy resolution in our experimental approach depends on the c.m. scattering angle), some rotational structures for the most dominant vibrational state v'=2 are still noticeable.

Also marked in Fig. 1 is the energetic onset for the formation of HF(v'=3) from the $F(^{2}P_{3/2}) + HD$ reaction, which occurs at $E_c = 1.16 \text{ kcal/mol}$. Yet, at $E_c = 0.4 \text{ kcal/}$ mol there is a prominent spike near zero kinetic energy release. Note that at 50 K only j=0 (82%) and j=1 (18%) of HD need to be considered. The rotational energy for j=1 is 0.26 kcal/mol which is far too small to be responsible for this spike. Similarly, a smaller peak at 0.4 kcal/mol can also be seen for $E_c = 0.8$ kcal/mol, which energetically does not correspond to any high *j*-state of HF(v'=2). Based on the energetic considerations, we ascribed them to $F^*({}^2P_{1/2})$ $+HD \rightarrow HF(v'=3) + D$ which is a thermal neutral process. This is an unequivocal evidence for the finite reactivity of $F^*({}^2P_{1/2})$, but its contribution to total reactivity is apparently small even in the threshold region. It should be stressed that this evidence rests only on thermochemistry, i.e., it is completely independent of the barrier height of the SW or HSW PES, and does not depend on the comparison with any dynamical calculation. It can also be seen that once the for-



FIG. 6. Collisional energy dependence of the HF product vibrational branching (upper panel) and the vibrational-specific excitation function (lower panel) for F+HD \rightarrow HF(v')+D. The "total" excitation function is obtained by connecting the data points from Fig. 1. The oscillations at higher energies are the experimental uncertainties. The small contributions from F*(${}^{2}P_{1/2}$) (the shaded area, upper panel) were included in the individual vibrational state-specific excitation functions (the lower panel).

mation of HF(v'=3) from the F(${}^{2}P_{3/2}$) reaction becomes energetically allowed, its population show a sudden boost. In particular, at $E_c = 1.18$ kcal/mol, the contributions to HF(v' =3) from $F({}^{2}P_{3/2})$ and $F^{*}({}^{2}P_{1/2})$ are most evident as two distinct features. Apparently, there is no delayed onset, i.e., no exit barrier, for the formation of HF(v'=3). Using a procedure similar to our previous work,³⁸ we partitioned the $P(E_t)$ distributions into product vibrational states. The results for 17 collisional energies ranging from 0.4 to 4.52 kcal/mol are summarized in Fig. 6. The vibrational branchings are given in the upper panel, and the vibrational statespecific excitation functions are in the lower panel. We first note that the overall contribution (not cross section) from $F^*({}^2P_{1/2})$ (i.e., sum of all v', in shaded area) is only a few percent over the entire energy range of this work. That is true even for $E_c < 1.1$ kcal/mol when the formation of HF(v' =3) from $F({}^{2}P_{3/2})$ is energetically closed.

It is noteworthy that very recently Nesbitt and his co-workers^{10,11} also reported the experimental evidence for a finite nonadiabatic reactivity of $F^*({}^2P_{1/2})$ in the reaction of $F+n-H_2$, which at first glance seems at variance with the earlier crossed-beam scattering results.^{2,3,5–7} The present work for $F({}^2P)$ + HD indicated, however, that there is actually no significant conflict among all experiments provided that there is no substantial isotope effects in $F^*({}^2P_{1/2})$ reactivities. First, the measurement of the HF(v',j') product state distribution by Nizkorodov *et al.*¹¹ was made only for



FIG. 7. As in Fig. 5, except for the $F+HD\rightarrow DF+H$ reaction.

v' = 3. Thus the nonadiabatic contribution from $F^*({}^2P_{1/2})$ in their experiment refers to v'=3 only, whereas in all other crossed-beam experiments, including the present one, they are referenced to the overall reactivity. Since HF(v'=3) is not the dominant product channel in $F+n-H_2$ even at low collision energy (e.g., see Ref. 2, Fig. 3 for $E_c = 0.68$ kcal/ mol), an appreciable $F^*({}^2P_{1/2})$ contribution to the formation of HF(v'=3) will still amount to a small contribution to total reactivity. Second, the evidence for nonadiabatic reactivity of $F^*({}^2P_{1/2})$ presented by Nesbitt's group^{10,11} depends upon the theoretical prediction near the threshold region. If the true barrier height for this reaction is, paradoxically, closer to that on the SW PES, as suggested by the present work, then the theoretical curve shown in the Fig. 7 of Ref. 11 should not be shifted upward by 0.38 kcal/mol. The resulted discrepancy between experiment and theory will be greatly reduced-although the finite nonadiabatic reactivity from $F^*({}^2P_{1/2})$ might still be evident.

Perhaps more intriguing in Fig. 6 is the collisional energy dependency of the vibrational branching. At low energies, $E_c \leq 1$ kcal/mol, most of reactive fluxes (>90%) are channeled into v'=2. As soon as v'=3 from $F({}^2P_{3/2})$ becomes accessible, its branching rises sharply with a concurrent drop for v'=2. At even higher energies, $E_c \geq 2$ kcal/mol, the branching for v'=3 declines gradually whereas v'=2 stays more-or-less constant following a small initial increase. As to the branchings for v'=1 and 0, both increase slowly with the increase in collision energies.

We will argue that this vibrational branching behavior could be another ramification of dynamical resonance in the is convrighted as indicated in the article. Reuse of AIP content is subject Dong, Lee, and Liu



FIG. 8. As in Fig. 6, except for the $F+HD \rightarrow DF(v')+H$ reaction.

integral cross sections. The low energy reaction is almost entirely governed by resonant scattering.^{24,37} The resonance state has been identified, in the local-mode picture, as (00°3) with three quanta of the H-F stretch and zero quanta of the H–D stretch and the bend. The dominance of the v'=2 formation follows the usual Δv -propensity rule in a vibrational predissociation process, which says the larger the $\Delta v = v_i$ $-v_f$, then the much less probable the vibrational predissociation.^{1,39} We will loosely term a decay process for $\Delta v \neq 0$ a Feshbach-resonance decay.⁴⁰ At higher energies $(E_c \ge 1.16 \text{ kcal/mol})$ the decay of this resonance state into HF(v'=3), which is called a shape-resonance decay,⁴⁰ becomes feasible. Hence, there is a competition between the Feshbach- and shape-resonance decays, which explains the abrupt rise in $\sigma(v'=3)$ around this energy. The resonances will be associated with larger partial waves with further increase in collision energies. The centrifugal barrier for shape-resonance decay becomes higher, lowering its probability, which could be the origin for the gradual decline for v'=3 after 2 kcal/mol. Consequently, a prominent peak shows up in both the state-specific excitation function and the collision energy dependence of the vibrational branching for HF(v'=3). Of course, there is the direct scattering component for $E_c \gtrsim 1.0$ kcal/mol on SW PES,²⁴ which also needs to be considered. A thorough QM analysis is necessary for a definite conclusion. Nevertheless, detailed analysis of our differential cross section data indeed suggest that v'=3 is totally dominated by resonant scattering at all energies, whereas v' = 0 - 2 consists of both contributions from resonant and direct scatterings for $E_c \gtrsim 1.1$ kcal/mol.⁴¹

TABLE I. Comparison of vibrational branchings^a for the F+HD \rightarrow DF(v') + H reaction at E_c =1.98 kcal/mol.

Method	v'=4	v'=3	v'=2	v'=1	v' = 0	F*
Expt. (Lee et al.) ^b	0.25	0.53	0.21	0.01		
Expt. (Polanyi et al.) ^c	0.26	0.43	0.23	0.08		
This work ^d	0.33	0.44	0.15	0.03	0.01	0.038
QM ^e	0.27	0.51	0.19	0.025		
QCT ^e	0.34	0.43	0.23	0.003		

^aDefined as $\sigma_{v'} / \Sigma_{v'} \sigma_{v'}$.

^bReference 3.

^cReference 41.

 ${}^{\mathrm{d}}E_c = 2.0$ kcal/mol.

^eFor HD (j=0) only.

2. F+HD \rightarrow DF(v')+H

The product $P(E_t)$ distributions for this channel are presented in Fig. 7. Again, the vibrational structures are readily resolvable. The resulted vibrational branchings are summarized in Fig. 8. Although the differential cross section measurements for this isotope channel were performed at only four different energies, Doppler profile measurements (//configuration) indicated a rather smooth variation over the entire energy range.⁴¹ Thus the main feature of the energy dependency of the vibrational branching should be captured. As is seen, in contrast with the HF(v') + D product channel, there is a more democratic distribution for this channel. Except for v' = 4 (the least exothermic state), all other vibrational states display a gradual increase in both the cross section and the branching with the increase in collision energies. The $F^*({}^2P_{1/2})$ contribution to this isotope channel is again rather small.

There are two previous experimental reports^{3,42} on the vibrational branching, both at a single collision energy. Table I summarizes the comparisons, along with the dynamical calculations on the SW PES. Qualitatively, all three experiments are consistent: an inverted distribution peaking at v'=3. Quantitatively, however, some discrepancies are noticed, which are beyond the experimental uncertainty $(\pm 3\%)$ for v'=2-4) of this work. The difference between the present work and the Lee's 1985 experiment rests mainly on the ratio of (v'=4)/(v'=3). On the other hand, Polanyi's result,⁴² for which the collision energy is less defined, indicated a slightly more even distribution for v'=2, 3, and 4. Compared to the dynamical calculations, the QM result (for j=0 only)¹⁸ is in excellent agreement with the Lee's experiment, whereas the QCT result⁴³ agrees better with the present one for v'=3 and 4. At first glance, these comparisons might be a bit confusing. First, in terms of total integral cross sections (Fig. 1), the QM result is certainly in better agreement with experiment than QCT. Yet, for vibrational branching QM yields a somewhat larger variance with ours than QCT. Second, while there are appreciable differences from the two dynamical calculations, both gave an equally good simulation to the experimental (DF+H) laboratory angular distribution.^{18,43} Clearly, neither the total excitation function nor the product laboratory angular distribution for this reaction provides a very stringent test of the calculation for a reaction attribute such as the vibrational branching. It is conceivable that the previous forward-convolution procedure³ might not yield a unique distribution as the present direct-mapping approach, which also has higher resolution. Alternatively, the rotational temperatures of the HD molecules in these experiments are not the same: the thermal one⁴² is at 300 K, the Lee's beam experiment is about 40 K (0.9 and 0.1 in j=0 and 1, respectively), and the present work is about 50 K (0.82 and 0.18 in j=0 and 1, respectively). If the dynamics of this reaction depends strongly on the initial rotational state, it could be the origin of these discrepancies. Similar effects have previously been noted for the F+D₂ reaction.⁵ In any event, it is recognized that the vibrational branching of this reaction is extremely sensitive to the fine details of the PES.^{43–45} Further work is warranted.

At last, it is interesting to note the appearance of a double-peaked kinetic energy distribution for DF(v'=3 and 4) at $E_c = 4.0 \text{ kcal/mol}$. A bimodal rotational distribution has also been reported recently for the backward scattered DF(v'=2 and 3) from $F+D_2$ at 2.07 kcal/mol.⁶ Due to space limitation, further discussion will be deferred to our future report on the state-resolved differential cross section.

IV. CONCLUSIONS

The reactions of $F+H_2$ and its isotopic variants stand at a unique position in the field of reaction dynamics. A number of important issues about this reaction are addressed in this work, from which several conclusions can be drawn.

First, at the level of detail of the integral cross section the transition-state properties including the barrier height of this reaction are well characterized by the SW PES, despite the fact that from the *ab initio* point of view the correct PES for the $F({}^{2}P_{3/2})$ reaction should be the HSW which raises the barrier by 0.35 kcal/mol. This conclusion corroborates the finding from the recent QM simulations of the other reaction attributes using the HSW PES.^{20–22}

Second, based on the excitation functions for $F+p-H_2$ and $F+n-H_2$, we speculated that a resonance may indeed exist for the $F+H_2$ reaction, in support of the original suggestion by Neumark *et al.*³ This conclusion seems in conflict with the classical line-of-center interpretation of the landmark 1985 scattering experiment drawn from the recent theoretical investigations,^{4,16,19} but the correct answer, classical versus resonance, could just be a question of degree.

Third, it is conjectured that the unusual energy dependence of the vibrational branching of the HF product provides another measurable signature for dynamical resonance in $F+HD\rightarrow HF+D$.

Finally, the nonadiabatic reactivity of the spin-orbit excited $F^*({}^2P_{1/2})$ atom is found to be small in F+HD over the entire energy range of this work. This conclusion is in corroboration of the other crossed-beam scattering experiments, ${}^{2,3,5-7}$ and of a most recent, full QM multisurface calculation. 23

ACKNOWLEDGMENTS

We are indebted to Professors R. T. Skodje, D. E. Manolopoulos, and F. J. Aoiz for stimulating discussions and

critical comments of this paper, and to Professor Y. T. Lee for his continued encouragement. The National Science of Council of Taiwan and the Chinese Petroleum Corporation supported this work.

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