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Spin-orbit effects in the reaction of $F(^2P)$ with H_2

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We report the first scattering calculations for the $F+H_2$ reaction based on *ab initio* potential energy surfaces (PES's) and an exact treatment of spin-orbit and Coriolis coupling. The probability of reaction of $F^*(^2P_{1/2})$ is less than 10% of that for $F(^2P_{3/2})$ and the overall features of the scattering are well represented by calculations on the lowest electronic PES. © 1998 American Institute of Physics. [S0021-9606(98)02638-5]

I. INTRODUCTION

Because of its experimental accessibility, the reaction of F with H_2 has become the paradigm for exothermic triatomic reactions.¹ Quantum-scattering calculations,²⁻⁶ as well as quasiclassical trajectory studies,^{6,7} based on the high-quality *ab initio* potential energy surface (PES) of Stark and Werner (SW),⁸ have successfully reproduced the major features seen in both the photodetachment spectrum of the FH_2^- ion^{2,9} and molecular-beam scattering studies of the $F+H_2$ (Refs. 10, 11) and $F+D_2$ (Ref. 12) reactions.

Approach of the H_2 molecule to the F atom splits the degeneracy of the 2P state. Two electronic states ($1^2A'$ and $1^2A''$; $^2\Sigma^+$ and $^2\Pi$ in linear geometry) correlate adiabatically with the ground-state atomic reactant ($^2P_{3/2}$) while a third state ($2^2A'$; $^2\Pi$ in linear geometry) correlates adiabatically with the excited-state atomic reactant ($^2P_{1/2}$).¹³ Of these, only the $1^2A'$ electronic state correlates with the electronic ground state of the products [$HF(X^1\Sigma^+) + H(^2S)$]. The two other electronic states correlate with electronically excited states of the products [$HF(a^3\Pi) + H(^2S)$] which are considerably higher in energy¹⁴ and consequently energetically inaccessible at low to moderate collision energies.

The presence of these three electronic states, as well as the sizable spin-orbit splitting in the F atom ($404\text{ cm}^{-1} = 1.15\text{ kcal/mol}$) raises two important questions: (1) what is the reactivity of the excited ($^2P_{1/2}$) spin-orbit state and (2) how well is the dynamics of the reaction described by calculations on a single, electronically adiabatic potential energy surface (PES).

Molecular beam, differential scattering studies^{10,12} indicate that the overall reactivity of the excited spin-orbit state is negligible at collision energies below 2 kcal/mol. (The barrier on the SW PES with the full spin-orbit Hamiltonian included is 1.9 kcal/mol.⁸) However, recent work by Nesbitt and co-workers¹⁵ suggests that the reactivity of the spin-orbit excited F atoms may be best explored by monitoring individual vibration-rotation levels of the HF products which

are energetically inaccessible for reaction of ground state F atoms.

Theoretical investigations of the role of the excited electronic surfaces in the $F+H_2$ reaction date back to the work of Tully.¹⁶ Previous scattering studies¹⁷⁻²⁰ which included one (or both) of the excited electronic states, have been subject to various approximations, both in the treatment of the dynamics as well as in the PES's and couplings (nonadiabatic, Coriolis, and spin-orbit) used.

We describe here an extension of earlier investigations by two of us.^{4,8} We have fit all three diabatic PES's in the entrance arrangement, and then carried out time-independent quantum scattering calculations of reactive transition probabilities. For the first time the electronic angular momenta of the reactants and the spin-orbit coupling has been included accurately and completely. Our work is closely related to the recent investigation, by Schatz and co-workers,²¹⁻²³ of spin-orbit effects in the symmetric $Cl+HCl \rightarrow ClH+H$ exchange reaction.

II. POTENTIAL ENERGY SURFACES AND COUPLING

Werner and co-workers⁸ used multireference configuration-interaction calculations with large atomic orbital basis sets to determine the three electronically adiabatic FH_2 PES's. These were then transformed to an approximate diabatic basis,^{8,24} in which the direction of the p hole is defined consistently with respect to the Jacobi center-of-mass vector \mathbf{R} .

The matrix of the interaction potential, in the 6×6 basis defined by the three diabatic projections of the p hole with respect of \mathbf{R} ($|\Pi_x\rangle$, $|\Pi_y\rangle$, and $|\Sigma\rangle$) and the two possible spin projections, can be described in terms of three electronically diabatic PES's, V_{xx} , V_{yy} , and V_{zz} .²⁵ It is the $|\Sigma\rangle$ state which correlates with the ground-state product channel. The transformation to the diabatic basis gives rise to a fourth function, V_{xz} , which is the coupling between the two states of A' symmetry. Similarly, the matrix of the spin-orbit operator is fully determined by two components. Details of the *ab initio*

TABLE I. van der Waals minima of lowest adiabatic F+H₂ PES's.^a

PES	R^b	D_e
SW	4.771	124.9
Present	4.795	123.9
Present with s.o. ^c	5.313	57.9

^aEnergies in cm⁻¹, distances in bohr.^bEntrance channel center-of-mass separation in Jacobi coordinates ($r = 1.4$ bohr, $\gamma = 90^\circ$).^cAdiabatic PES calculated with inclusion of the spin-orbit Hamiltonian.

calculations are given in Ref. 8. All four diabatic PES's and the two spin-orbit terms were fit by multiparameter functions.

Inside the barrier the lowest electronically adiabatic surface was smoothly merged to the SW PES, and the excited surfaces were harmlessly extrapolated to high repulsive plateaus. Thus, outside the reactant arrangement, the description of the FH₂ system is unchanged from the original SW fit, with the addition of two high-energy electronic states.

In the absence of spin-orbit coupling, the F+H₂ barrier and van der Waals minima on the lowest adiabatic PES from the present fit are virtually identical to those predicted by the SW PES (see Table VII of Ref. 8). At the barrier the spin-orbit coupling has only a small effect on the Σ state, because the Π states lie much higher in energy.

Asymptotically, the spin-orbit coupling results in an increase in the height of the barrier,^{6,8,9,21} with respect to the F+H₂ reactants, by 131 cm⁻¹ (0.374 kcal/mol), $\approx 1/3$ of the F atom spin-orbit splitting. The position of the barrier is unchanged. In addition, the spin-orbit coupling significantly alters both the depth and position of the van der Waals minimum, as can be seen in Table I. This will certainly have an impact on the role of entrance channel resonances in the reactivity at low energies.²⁶

Asymptotically, the Σ state and the Π state with $\Omega = 3/2$ correlate with F(²P_{3/2})+H₂, while the Π state with $\Omega = 1/2$ correlates with F(²P_{1/2})+H₂. Both the electrostatic interaction potential and the spin-orbit Hamiltonian couple the ground and excited spin-orbit channels, even in the absence of rotational (Coriolis) coupling.

III. SCATTERING CALCULATIONS

The reactive scattering calculations were carried out in a manner similar to that described by Schatz.²¹⁻²³ We used a close-coupled, time-independent method, expanding the scattering wave function as a product of electronic-vibrational-rotational states for each of the arrangement channels. The calculations were done with an extension of a computer code described previously by one of us.^{4,5}

In the F+H₂ arrangement the expansion of the wave function involves all six electronic states. However, in the HF+H arrangement channel the 2²A' and 1²A'' states correspond to HF(*a*³Π)+H. Since the HF(*a*³Π) state lies >80 000 cm⁻¹ above the ground electronic state,¹⁴ we did not include the higher two electronic states in the product arrangement channel. In addition, we used correct parity-

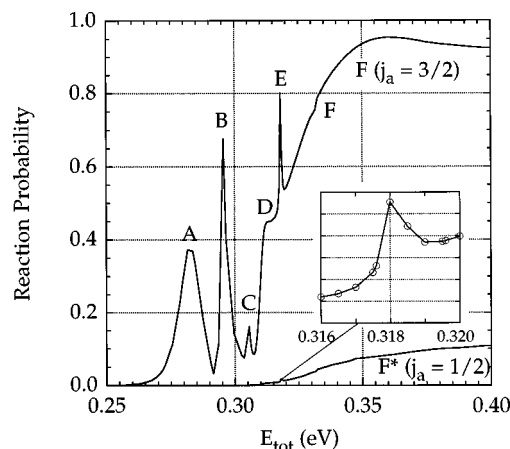


FIG. 1. Total F+H₂($j=0$) reaction probability [Eq. (1)] for $J=0.5$. The inset panel displays in more detail the resonance structure in the F(²P_{1/2}) reaction probability. The zero of energy is taken to be the weighted average of the two F atom spin-orbit states. The resonance features marked "A"–"F" are discussed in more detail in Ref. 4.

adapted linear combinations of the primitive rotation-vibration-electronic basis functions as well as an exact treatment of all Coriolis couplings.

At the end of the propagation, the S matrix was obtained in a coupled basis,^{21,23} in which the spin-orbit operator is diagonal and the atomic states in the reactant arrangement are labeled by the total electronic angular momentum of the atom, j_a , and its projection on \mathbf{R} , ω .

Figure 1 displays the total, degeneracy-averaged reaction probabilities for reaction of H₂($j=0$) with F(²P_{3/2}) and F(²P_{1/2}) as a function of the total energy and for a total angular momentum $J=1/2$, which is the lowest allowed value. These reaction probabilities should be comparable to the $J=0$ reaction probabilities obtained in a single-surface treatment in which electronic angular momentum is ignored. However, in contrast to this simpler situation, to determine reaction probabilities out of $j=0$, both parity blocks occur here for $J=1/2$. In terms of the S matrix the probabilities plotted in Fig. 1 are defined by

$$P_{j,j_a}^J(E_{\text{tot}}) = \frac{1}{(2j+1)(2j_a+1)} \times \sum_{k,\omega,\eta,f} |S^{JK}(jkj_a\omega\eta \rightarrow f; E_{\text{tot}})|^2, \quad (1)$$

where the summation extends over all energetically allowed final states $|f\rangle$ associated with the product arrangement channel, as well as all allowed values of the entrance channel body-frame projection quantum numbers k and ω , and the parity index η .

The probabilities for reaction out of the ground spin-orbit state of the F atom are virtually identical to those obtained from single surface calculations with the SW PES (see Fig. 10 of Ref. 4), even to the positions of the resonance features marked "B" through "F". These correspond to Feshbach resonances in the product arrangement.⁴ Since the new PES and the SW PES are identical in the product arrangement, it is understandable that both the position and shape of these resonance features are identical. Feature "A"

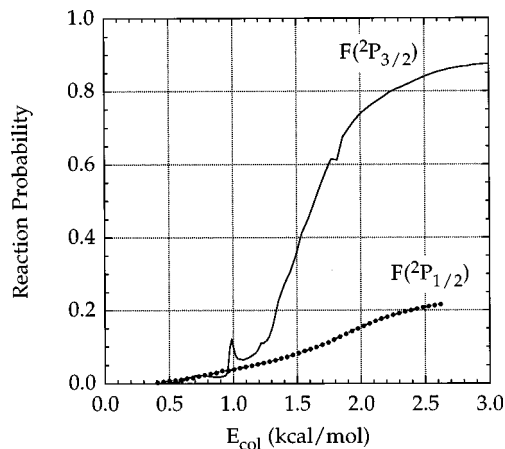


FIG. 2. Total $F+H_2(j=1)$ reaction probability [Eq. (1)] for $J=0.5$, plotted as a function of the initial collision (kinetic) energy.

is due to a direct scattering state in the threshold region and is sensitive to the energetics and topology of both arrangement channels. This feature is shifted very slightly (2.5 meV) from where it occurs in the single-surface calculations.⁴ This shift may be an indication of the slight differences in the PES's in the entrance channel which result from the inclusion of spin-orbit coupling (see Table I and also compare with Table I of Ref. 6). Since the number of *ab initio* points in the reactant arrangement used in the present work is considerably larger than in the earlier SW fit,⁸ we anticipate that the present fitted PES's will be more accurate in the entrance channel.

Because the $F(^2P_{1/2})$ channel is closed at total energies below 0.304 eV, the resonance features "A"–"D" do not show up in the reaction probabilities for the F^* channel. However, we do see slight evidence of features "E" (see the inset plot in Fig. 1) and "F."

We also observe in Fig. 1 that the probabilities for reaction of $F(^2P_{1/2})$, although certainly non-negligible, are at most $\approx 10\%$ of the probabilities for reaction on the adiabatically allowed pathway out of the ground F atom channel.

Figure 2 displays the $J=0.5$ probabilities for reaction with H_2 in $j=1$ (ortho- H_2). Here, in contrast to Fig. 1, we plot the probabilities as a function of the initial collision (kinetic) energy, rather than the total energy, which would allow a more direct comparison with experiment. As discussed earlier by Castillo *et al.*,⁴ the resonance structure is greatly reduced for reactions involving *o*- H_2 , although traces of the strong Feshbach resonances are still apparent. Again, the reaction probabilities for the F^* channel are small. Even at low collision energies, although the $^2P_{1/2}$ channel has greater internal energy, the probability of reaction out of this state is at most comparable to the probability of the adiabatically allowed reaction out of the lower spin-orbit state.

IV. DISCUSSION

The present calculations now allow us to answer the two questions raised in the Introduction. First, the overall reactivity of the excited (2P) spin-orbit state of F, which is not allowed adiabatically, is small (at most 10% of the reactivity of the ground spin-orbit state²⁷). Secondly, the overall dy-

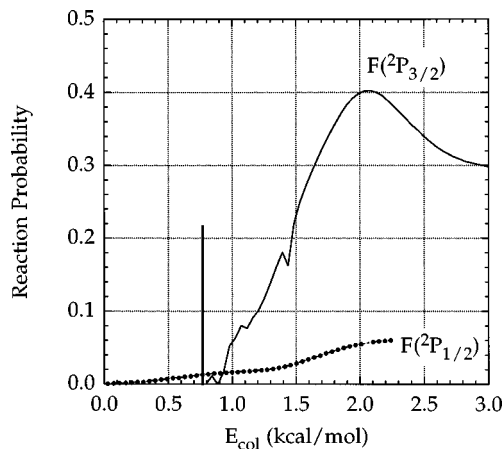


FIG. 3. Probabilities ($J=0.5$) for the reaction of $F+H_2(j=1)$ to produce HF products in $v'=3$, plotted as function of the initial collision energy. The vertical bar marks the threshold for appearance of $v=3$ products in the reaction of $F(^2P_{3/2})$ with $H_2(j=1)$.

namics of the $F+H_2$ reaction will be well described by calculations on a single, electronically adiabatic PES. This contradicts an earlier prediction,²⁰ based on quantum scattering calculations using more approximate PES's.

Because the HF $v'=3$ vibrational manifold is endoergic with respect to both the $j=0$ and $j=1$ levels of H_2 ($v=0$), experiments such as those of Nesbitt and co-workers,¹⁵ which detect HF products in $v'=3$, may provide a means to observe the reaction of the excited spin-orbit state of the F atom. To illustrate this, Fig. 3 displays the $J=0.5$ probability for the reaction of H_2 ($j=1$) to produce HF products in $v'=3$, summed over all product rotational levels. We observe a sharp break in the reaction probability as the threshold for the adiabatically allowed reaction of the ground spin-orbit state is crossed.

The endoergic of the HF $v'=3$ vibrational manifold with respect to H_2 ($v=0$, $j=1$) predicted by the present PES's ($\Delta E_0=0.79$ kcal/mol), which are based on the *ab initio* calculations of Stark and Werner,⁸ is somewhat larger than the spectroscopically and thermochemically derived value ($\Delta E_0=0.18$ kcal/mol). Nonetheless, the study of the energy dependence of the cross section for formation of particular rotational levels in HF ($v'=3$) may well reveal similar, or more dramatic, threshold behavior which would demonstrate unambiguously the relative reactivity of the excited spin-orbit state of the F atom.

Further calculations, including the determination of full integral cross sections, are in progress and will be reported shortly, along with the complete description of the excited PES's. This investigation will explore in more detail possible signatures of the adiabatically forbidden F^*+H_2 reaction.

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