

LETTER

A Global *ab initio* Potential Energy Surface for $F+H_2\rightarrow HF+H$ Chuan-xiu Xu^a, Dai-qian Xie^{a*}, Dong-hui Zhang^{b*}

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A global three dimensional potential energy surface for the $F+H_2\rightarrow HF+H$ reaction has been developed by spline interpolation of about 15,000 symmetry-unique *ab initio* points, obtained from the multi-reference configuration interaction level with Davidson correction using the aug-cc-pV5Z basis set. In the entrance channel the spin-orbit coupling energy is also included.

Key words: Potential energy surface, Multi-reference configuration interaction, Spin-orbit coupling, FH_2

The reaction $F+H_2\rightarrow HF+H$ is a prototype in the field of gas phase reaction dynamics and has been extensively studied both experimentally and theoretically over the past decades. Recently, Liu and coworkers measured the integral cross section of $F+HD$ and found a reactive resonance appeared in the integral cross section for the reactive channel [1]. Very recently, Feshbach resonances in the $F+H_2\rightarrow HF+H$ reaction were observed by Yang and collaborators with the highly sensitive H atom Rydberg tagging time-of flight method [2]. In 1996, Stark & Werner calculated the first global *ab initio* potential energy surface (SW PES) for $F+H_2$ [3], which correctly described the transition state for the $F+H_2$ reaction. Dramatic validation of the accuracy of the surface in the region of the transition state was provided by calculations of the FH_2^- ion photoelectron spectrum [4] which was in excellent agreement with experiments by the Neumark group [5]. A number of quantum-scattering calculations [5-9], as well as quasi-classical trajectory studies on the SW potential [6,10] were performed to investigate the dynamical properties of the FH_2 system. These theoretical studies have successfully reproduced the major features of the reactions. However, the limitations of SW PES have been pointed out in the reactive scattering calculation of the $F+HD$ reaction, for which fully converged quantum mechanical calculations [9] did not reproduce satisfactorily the recent beam experiments by Liu and co-workers [1].

An important feature of the fluorine as a reactant is its open-shell nature and presence of fine-structure splitting due to the spin-orbit coupling which splits the 2P state of the open shell F atom into $F(^2P_{1/2})$ and $F(^2P_{3/2})$ states. The splitting between the two states

is about 400 cm^{-1} . Therefore, the coupling between the two states can not be neglected in the entrance channel. Two electronic states ($1^2A'$ and $1^2A''$, $^2\Sigma^+$ and $^2\Pi$ in linear geometry) correlate with the ground-state atomic reactant ($^2P_{3/2}$), while a third state ($2^2A'$, $^2\Pi$ in linear geometry) correlates with the excited-state atomic reactant ($^2P_{1/2}$). While only the $1^2A'$ electronic state leads to the electronic ground state of the products $HF(X^1\Sigma^+)+H(^2S)$. In this communication, we concentrated on the ground $1^2A'$ electronic state of $F+H_2$.

The *ab initio* calculations for the ground electronic state of FH_2 were performed using the internally contracted multi-reference configuration interaction method with the Davidson correction (icMRCI+Q) [11], as implemented in the MOLPRO package [12]. We calculated the energies at every point with a series of basis sets of the correlation consistent valence 5-Zeta (aV5Z) of Dunning [13]. All the reference wave functions were taken from the natural orbitals obtained from a state-averaged complete active space self-consistent field (CASSCF) wave function for equally weighted $1^2A'$, $2^2A'$ and $1^2A''$ states. 7 active electrons and 9 active orbitals were used. The 1s and 2s orbitals for the fluorine atom were kept doubly occupied but fully optimized during the CASSCF procedure. The MRCI+Q calculation was then carried out to generate the electron correlation energy. The total number of contracted configurations in this calculation was about 7 million. All calculations were performed in C_s symmetry. We selected a non-uniform direct product grid in the internal coordinates (r_{HF} , r_{HH} , θ) to construct a global PES for the system, where r_{HF} is the distance between the H atom and the F atom, r_{HH} is the distance between the two H atoms, and θ is the enclosed bond angle. We have chosen relatively dense grids for the two radial coordinates with 27 points covered the H-F radial coordinate from 1.2 to 11.0 a_0 , and 28-35 points in H-H radial coordinate from 0.7 to 13.0 a_0 . In the angle co-

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ordinate, 19 points ranging from 0° to 180° were used. This set of grids thus gives about 15,000 symmetry-unique points. Finally, a three-dimensional cubic spline interpolation was employed to yield a global PES for the system. For collinear geometries the F+H₂ asymptote correlates with a ²Σ⁺ and a ²Π state. These states are strongly mixed by spin-orbit coupling in the asymptotic region, which leads to a splitting of the F(²P_{1/2}) and F(²P_{3/2}) components. The spin-orbit matrix elements were computed using the Breit-Pauli Hamiltonian using internally contracted multireference configuration interaction wave functions for the lowest three electronic states with the aug-cc-PVQZ basis set (excluding g functions) [14].

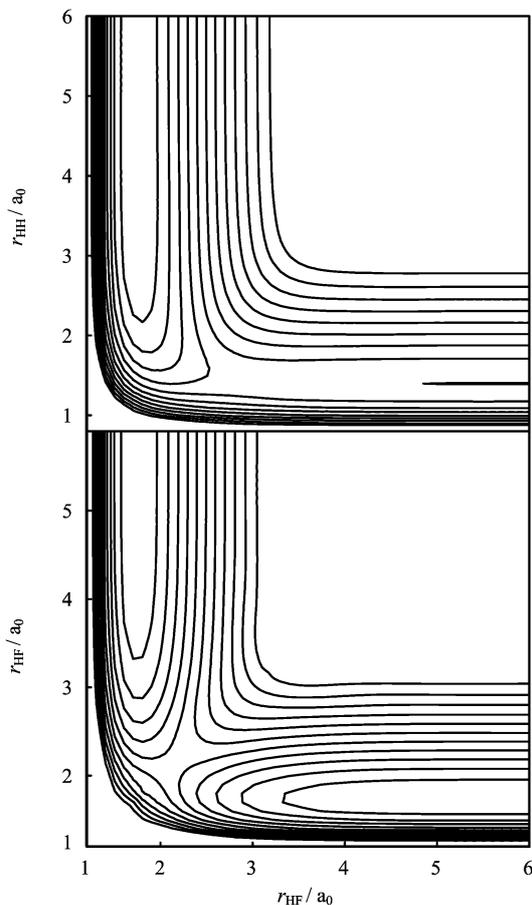


FIG. 1 Upper panel is the contour plot of the F+H₂ PES for collinear geometries as a function of the r_{HH} and r_{HF} distances. Lower panel is the contour plot of the collinear PES for the H'+HF→H'F+H exchange reaction as a function of the two r_{HF} distance. Contours are spaced by 0.35 eV.

The reaction of F+H₂→HF+H is the paradigm for exothermic triatomic reaction. The reaction starts with a rather flat ascent in the entrance channel region until the barrier is present. After the barrier it falls off steeply into the exit valley. In the new PES, the reaction exothermicity is found to be 132.76 kJ/mol, which is in better agreement with the observed of 132.63 kJ/mol than the previous theoretical value of

130.96 and 132.63 kJ/mol from the SW [3] and HSW [6] PESs. Table I further compare the barrier properties. The upper panel of Fig.1 plots the contours for the collinear reaction, in which barrier is clearly visible. One can see from Table I that the HH distance at the barrier is 1.442 a_0 , very close to the H₂ equilibrium distance of 1.402 a_0 . Table I also gives the comparison for the bent transition state. The present potential shows a bent transition state at $\theta=119^\circ$ with a barrier height of 7.98 kJ/mol, which is in good agreement with the results of HSW PES.

TABLE I Comparison of the barrier properties for F+H₂ reaction.

	r_{HF}/a_0	r_{HH}/a_0	$\theta_e/(\circ)$	$E/(\text{kJ/mol})$
Collinear barrier				
SW [3]	2.95	1.442	180	8.03
HSW [6]	2.95	1.442	180	9.57
This work	2.94	1.442	180	9.40
Bend barrier				
SW [3]	2.92	1.457	119	6.39
HSW [6]	2.91	1.458	118	7.98
This work	2.91	1.457	119	7.98

The exchange barrier for the H'+HF→H'F+H has also been located. The lower panel of Fig.1 displays the collinear potential energy surface as a function of two r_{HF} . One can see a barrier at a distance of $r_{\text{HF}1}=r_{\text{HF}2}=2.151 a_0$ with a barrier height of 174.39 kJ/mol relative to the HF+H asymptote.

The depths and the geometries of the van der Waals minima are compared in Table II between our new PES and the previous potentials. The upper panel of Fig.2 shows the entrance channel of F+H₂ reaction with and without the effect of the SO coupling. The effects of the spin-orbit interactions at the van der Waals geometries are essentially to pull the well to a larger r value and halve the depth. The geometries from the new PES are very similar to that in the HSW PES which also included the spin-orbit corrections. A comparison of the one-dimensional plot with a fixed HF distance of 1.74 a_0 is shown in the lower panel of Fig.2. One can see a minimum geometry which is located at $r_{\text{HF}}=1.74 a_0$ and $r_{\text{HH}}=4.26 a_0$. The similar geometry has been found

TABLE II Comparison of the van der Waals minima of the ground F+H₂ PES.

	r_{HF}/a_0	r_{HH}/a_0	Well depths/ cm^{-1}
In the entrance channel			
SW [3]	4.89	1.40	129.41
HSW [6]	5.39	1.41	62.96
This work	5.46	1.40	37.72
In the exit channel			
SW [3]	1.74	4.19	87.44
HSW [6]	1.74	4.19	87.44
This work	1.74	4.26	108.76

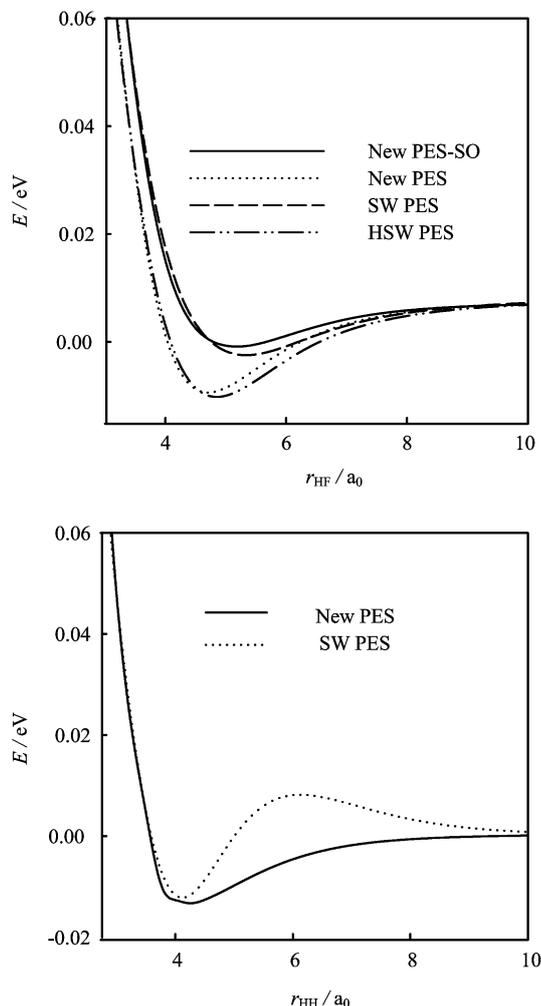


FIG. 2 Upper panel is the comparison of one-dimensional potential cuts for $F+H_2$ channel at $\theta=90^\circ$ and $r_{HH}=1.44 a_0$ for the new, SW and HSW PESs. Lower panel is the comparison of one-dimensional potential cuts for $HF+H$ channel at $\theta=180^\circ$ and $r_{HF}=1.74 a_0$ for new and SW PESs.

on the SW and HSW PESs. The well depth in the exit channel is about 108 cm^{-1} which is deeper than that on the SW PES.

To conclude, we have determined an accurate global potential energy surface for the electronic ground state of $F+H_2$ with the state-of-the-art *ab initio* calculations. The quantum scattering studies, based on this new PES, can reproduce very well the recent observed

Feshbach resonances [2]. We believe this new potential could provide a reliable platform for studies of the reaction dynamics for the reaction of $F+H_2 \rightarrow HF+H$.

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