$F + H_2 \rightarrow FH + H$ Potential Energy Surface: Construction of the Reference Configuration State Function Space and MR-ACPF-2 Results

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ABSTRACT: A new electronic configuration reference space (subsequently used in multi-reference averaged coupled pair functional (MR-ACPF) or multi-reference configuration interaction singles and doubles [MR-CI(SD)] level treatments of electron correlation) is determined using the aug-cc-pVQZ basis set as a step toward constructing a new potential energy surface (PES) for the $F + H_2 \rightarrow FH + H$ reaction. We use our new reference space to calculate several chemically important properties (e.g., barriers, exothermicity, van der Waals wells) of the $F + H_2$ PES. We obtain nonrelativistic barrier heights of 1.32 kcal/mol^{-1} (bent) and 1.67 kcal/mol^{-1} (collinear) that are ~0.2–0.3 kcal/mol^{-1} lower than those obtained from the current best PES. Our nonrelativistic value for the exothermicity is 32.45 kcal/mol^{-1}, which is 0.7–1.1 kcal/mol^{-1} higher than the values obtained from some other PESs and 0.45 kcal/mol^{-1} higher than the experimental value. The van der Waals wells we find are slightly deeper (0.05 kcal/mol^{-1}) than the wells on the other PES. The ≈1-kcal/mol^{-1} magnitude of the differences among barrier heights, exothermicities, and well depths, obtained in our work and using the most reliable current PESs suggest that to obtain a three-dimensional (3D) PES for the $F + H_2 \rightarrow FH + H$

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accurate to 0.2 kcal/mol^{-1}, we will have to use even higher-level methods (e.g., explicitly correlated wave functions) and include relativistic corrections. We intend to do so in the next phase of this effort that is currently under way. Int J Quantum Chem 106: 1516–1527, 2006

Key words: potential energy surface; exothermicity; barrier height; active space; ACPF

1. Introduction

The F + $H_2 \rightarrow$ HF + H chemical reaction (including isotopomers) has long been the subject of much experimental and theoretical research. Total and angular cross sections, rates, and product vibration-rotation state populations are the primary quantities that have been probed for this reaction. Despite the presence of only three atoms, several experimental and theoretical advances had to occur to attain even quasi-quantitative agreement between the findings of theory and experiment, as we now summarize.

For many years, theorists have had serious difficulty in reproducing a qualitatively correct picture of the experimental results [1–6] for this reaction. This has been largely due to the lack of sufficient computer power to perform very accurate quantum scattering calculations, but it also arose from the lack of a sufficiently high-quality potential energy surface (PES). The early PESs for this reaction were semi-empirical [7, 8]. Bender et al. [9] calculated the first ab initio PES using the configuration interaction (CI) method at the single-excitation level (CIS). After an early period of encouraging results in the calculation of an ab initio PES, a period of disappointment followed, the history of which is surveyed by Schaefer [10]. Truhlar and coworkers then made a significant advance by finding and characterizing the bent transition state [11, 12] using a scaled electron correlation (SEC) [13] approach. Bauschlicher et al. [14, 15] then improved matters by using a large enough orbital basis and a Davidson-corrected multi-reference configuration interaction (MR-CI+Q) wave function to include the effect of higher than double excitations on the correlation energy.

Meantime, Lee and coworkers [16–18] were able to experimentally determine the product Hartree–Fock (HF) molecule's vibrational state differential cross sections for this reaction. Also, Neumark and coworkers [19–21] were able to determine, by analyzing vibrational structure in the FH_2^- photodetachment spectroscopy, that the transition state was indeed bent.

Subsequently, in 1996, Stark and Werner (SW) [22] calculated a new and more accurate ab initio PES, using the internally contracted multi-reference configuration-interaction method (IC-MRCI) [23]. Quasi-classical trajectory calculations [24–27] as well as quantum mechanical scattering calculations [28–34] on the SW surface produced cross sections and HF vibrational state populations results in reasonable but not quantitative agreement with the experimental data.

To further improve the agreement with the experimental FH_2^- photo detachment spectrum, Hartke and Werner [35] added to the SW surface spin-orbit corrections in the F + H_2 reactant channel. The new spin-orbit corrected PES (labeled HSW) increased the barrier height by 0.38 kcal/mol^{-1} relative to the SW surface, decreased the exothermicity by 0.38 kcal/mol^{-1}, and shifted the van der Waals well toward the reactants in the F + H_2 channel. Although the introduction of the spin-orbit coupling did improve the theoretical simulation of the photodetachment spectrum of the FH_2^- anion, the agreement between the experimental product vibrational populations and the corresponding quantum mechanical and quasi-classical scattering results based on the HSW surface were not better than those results from the SW surface [30, 36–38].

Although the possible nonadiabaticity of the F + H_2 reaction had already been researched during the mid-1970s by Tully [39] and other investigators [40] a few groups suggested that the deficiencies in the scattering results obtained from the SW and HSW surfaces might originate in the lack of the nonadiabaticity [41, 42] in the theoretical treatments. Later, Nizkorodov et al. [43, 44] provided experimental evidence that certain HF product states could only be accessed at low collision energies by the excited spin-orbit state of the F atom ($^2P_{1/2}$). Alexander et al. [45, 46] calculated the three lowest PESs that correlate asymptotically to F ($^2P_{3/2}$) and $^2P_{1/2}$ (we denote the results obtained ASW) using the IC-MRCI method but rescaled to produce the barrier of the SW surface. From the quantum mechanical scattering calculations performed on the ASW surface, Alexander et al. [46] concluded that the reaction on the $^2P_{1/2}$ excited state indeed plays a small role, but they stated that "even fine details of the dynamics of the H_2 + F reaction will be well described by calculations on a single PES." Zhang et al. [47] came to the same conclusion when they investigated the role of nonadiabatic couplings when studying the F + D_2 reaction using the ASW surface. In summary, the overall reactivity of the excited state of F was found to be at most 25% of that of the ground spin-orbit states, so it should be sufficient to focus on the lowest Born–Oppenheimer surface.

In recent years, the existence of a reactive resonance in the integral cross section [48–50] has finally been demonstrated by a combination of theory and experiment for the F + HD reaction, although this idea had already been introduced by several researchers in the past [16, 17, 51, 52]. The agreement between the theoretically simulated excitation function (σ) for F + HD → HF + D, and the experimental result has been disappointing. Although the simulated results based on the ASW [53] surface are in better agreement with the experiment than those based on the SW [48] surface, Tzeng and Alexander still need to shift the collision energies by ≈0.35 kcal/mol^{-1} to obtain a better comparison with the experimental data. This is an indication of persistent inaccuracies in the ASW and SW surfaces [53]. Another discrepancy in the agreement between experiment and theory is seen in the fact that compared with the experimental cross sections, certain experimental rotational product channels are severely underpopulated [e.g., HF ($v = 3, j = 3, 4$)] or completely closed [e.g., HF($v = 3, j = 5$)] when the SW PES is used in scattering calculations. Chapman et al. [54] traced these discrepancies to errors in the SW PES, especially its exothermicity.

In summary, the latest experimental and theoretical results show that the SW surface (including the ASW and HSW refinements) can render quasi-quantitative results, but to achieve better connection between the experimental data and theoretical predictions, a more accurate surface is needed. This requires a more accurate description of electron correlation than included in the SW surface. The r_{12} method of Kutzelnigg and coworkers [55, 56] has proved excellent and reliable for handling high-level dynamical correlation effects (for a recent extension to account for nondynamical correlation, see Refs. [57–59]). In a first step toward constructing a new and more accurate PES for the F + H_2 → FH + H reaction, we studied the HF molecule using an explicitly correlated multi-reference averaged coupled pair functional (MR-ACPF) method. Our results (vibrational levels and dissociation energy) were in essentially perfect agreement with the experimental values [60]. Results of similar quality were obtained in earlier studies of N_2 [61], He_2 [62], and Ne_2 [63].

In the present work, we carefully investigate how to construct a reference electronic configuration space that is balanced along the full F + H_2 → HF + H PES, paying special attention to avoid artificial symmetry breaking, and to an accurate characterization of van der Waals wells on the entrance and exit channels as well as the transition-state region of the PES. We demonstrate that the use of the resulting reference space (even without explicit correlation) provides results within the range of accuracy of the SW and ASW surfaces, which suggests that our subsequent r_{12}-correlated PES may improve the accuracy enough to resolve many of the persisting differences between theory and experiment for this reaction.

The organization of this article is as follows. In Section 2 we discuss the method of investigation and our notation. Section 3 presents the results and discussion of the different reference configuration active spaces (AS), showing how we select the particular AS we choose. In Section 4 we use the new AS to compute at the ACPF- and CI-level properties of H_2 and HF, as well as the van der Waals wells, the linear-constrained and bent transition states, and the exothermicity of the F + H_2 reaction.

2. Methods and Notation

We evaluated the quality of each electronic configuration AS by its barrier height $E^\ddagger$ at the linear transition state and its electronic exothermicity (ΔE). The exothermicity and the barrier have been shown to be very sensitive to the choice of the correlation method and, in particular, to the choice of the reference space. We also monitored the presence of symmetry breaking and exclude AS choices that produce non-negligible artifacts (i.e., $\geq 10\ \mu E_h$, with E_h denoting 1.0 Hartree of energy). We used Dunning's aug-cc-pVQZ basis set [64], which we demonstrated earlier to be capable of yielding results to the accuracy we desire (i.e., <1.0 kcal/mol^{-1}, using non-r_{12} methods and 0.1–0.2 kcal/mol^{-1} using r_{12} methods).

The molecular orbitals were either optimized in a multi-configurational self-consistent field (MC-SCF) calculation or taken partially or completely from a MCSCF calculation performed using another active space. As usual, the redundancies within the active orbital space were resolved by diagonalizing the generalized Fock matrix (denoted **Q** by Shepard et al. [65]), and the MCSCF energies were converged to a precision of 10^{-10} E_h.

In our multi-reference averaged coupled-pair functional (MR-ACPF-2) and MR-CI(SD) calculations, single and double excitations were generated from all the doubly occupied and active orbitals in the reference wave function unless otherwise specified. The ACPF-2 and CI energies were converged to a precision of 1 μE_h. All electronic structure calculations were carried out with the Amica [66] program suite, which is based on the Columbus [67] program package. Finally, the lowest-energy orbital was kept frozen in all the ACPF-2 and CI calculations.

The geometry of the F + H_2 system can be expressed using the three interatomic distances, r_{FH}, $r_{\mathrm{HH'}}(\equiv r)$, and $r_{\mathrm{FH'}}$, although in Section 4 of this article, we use two additional notations. The transition state geometry can be described using the two interatomic distances r_{FH}, $r_{\mathrm{HH'}}$, and the angle θ ($\theta = 0$ corresponds to a linear structure). The geometry of the reactant channel, where F approaches the H_2 molecule, is described by the Jacobi coordinates: r ($\equiv r_{\mathrm{HH'}}$), R (the distance from the F atom to the center of mass of H_2), and the angle φ formed by the vectors associated with r and R.

In examining various choices of AS configurations, we focused our calculations near three geometries [22] known to lie along the collinear-constrained reaction path studied by SW: the reactant asymptote ($r_{\mathrm{FH}} = 100.00$ a_0; $r_{\mathrm{HH'}} = 1.4008$ a_0 [68]), the linear transition state ($r_{\mathrm{FH}} = 2.95$ a_0 [22]; $r_{\mathrm{HH'}} = 1.442$ a_0 [22]), and the product asymptote ($r_{\mathrm{FH}} = 1.7328$ a_0 [60]; $r_{\mathrm{HH'}} = 100.00$ a_0), but we also considered geometries near the bent transition state.

The notation ($klmn/xywz$) is used to denote an AS in the C_{2v} symmetry with k, l, m, and n orbitals of the irreducible representation a_1, b_1, a_2, and b_2, respectively. Within this set, x, y, w, and z orbitals of the irreducible representation a_1, b_1, a_2, b_2 are inactive (meaning that these orbitals remain doubly occupied in the reference wave function). The corresponding notation in the C_s symmetry is (pq/rs), where p and q are all the number of orbitals in the a' and a'' irreducible representation, and r and s of these orbitals are inactive in the reference wave function. Of course, in the ACPF-2 and CI calculations, all single and double excitations out of the internal orbitals (unless specified otherwise), are then included, so the total number of configuration state functions can be very large. Finally, in Tables I and II we add another label $w|v$ in listing our results. The number w corresponds to the value (e.g., energy, number of references) obtained in C_{2v} symmetry, the latter to the value obtained in the C_s symmetry.

3. Active Space Choices

In this section, we present the energies of H_2 + F, HF + H and the constrained linear transition state obtained using a variety of reference configuration state function (CSF) spaces. Of course, these sets of electronic configurations represent those out of which further orbital excitations occur in the subsequent CI or ACPF-2 wave functions. In the first set of reference spaces (Table I), the two lowest-energy (in the MCSCF Fock matrix) molecular orbitals (corresponding to the F(1s) and F(2s) orbitals at the F + H_2 geometries) are kept inactive (meaning doubly occupied in all reference CSFs). This minimal complete active space (CAS) for this 11-electron system is labeled 5101/2101 in C_{2v} symmetry, or 61/31 in C_s symmetry. In the F + H_2 reactant asymptote, the three active orbitals correspond to the $H_2(1\sigma_g)$, $H_2(1\sigma_u)$, and F($2p_z$) orbitals. In the product limit, the active orbitals are the bonding and anti-bonding combination of F($2p_z$) and H(1s) orbitals, and the 1s orbital on the distant H. In this particular AS, the F($2p_x$,$2p_y$) orbitals are kept inactive, but in subsequent reference spaces this constraint is removed.

Making the F($2p_x$,$2p_y$) orbitals active results in the (5101/2000|61/20) AS, in which only the F(1s) and F(2s) orbitals remain inactive. From the data presented in Table I, we note significant changes in moving from the first to the second AS. For example, in the HF + H product asymptote, the MCSCF energy (unless specified, we include all configurations, so we are performing CAS calculations) in C_s symmetry differs from the C_{2v} result by almost 200 μE_h. Moreover, the ACPF-2 and CI energies of the reactant, linear barrier, and product calculated in the C_{2v} point group differ from the energies obtained in the C_s point group by as much as 2 mE_h. These artificial symmetry breaking effects therefore exclude these choices of AS, so we have to move to another choice.

It is well known that the F atom acquires partial F^- character [22, 69] during the F + H_2 reaction and that an accurate description of the F(2p) orbitals'

TABLE I
Energies of the F + H_2 system at the reactant, linear transition state, and product geometries, as well as the linear barrier height and the electronic exothermicity ΔE.*

				Lin. TS.			
			F + H_2	$-(100. + x/1000)/E_h$	FH + H	Lin. Barr.[b]	ΔE[b]
AS	No. ref[a]	Method	$C_{2v}\|C_s$	$C_{2v}\|C_s$	$C_{2v}\|C_s$	$C_{2v}\|C_s$	$C_{2v}\|C_s$
5101/2101 61/31	8|8	CASSCF	561.206|561.206	545.789|545.789	592.051|592.051	9.675|9.675	19.355|19.355
		ACPF-2[1,c]	822.345|822.345	818.886|818.886	872.861|872.861	2.171|2.171	31.699|31.699
		CI[1,c]	813.777|813.777	808.966|808.966	863.666|863.666	3.019|3.019	31.306|31.306
		ACPF-2[1,d]	821.396|821.396	818.276|818.276	872.373|869.823	1.958|1.958	31.989|30.388
		CI[1,d]	812.298|812.298	808.001|808.001	862.757|859.425	2.696|2.696	31.664|29.573
5101/2000 61/20	14|24	CASSCF	561.206|561.206	545.869|545.869	592.537|592.730	9.625|9.624	19.660|19.782
		ACPF-2[1,c]	822.559|822.689	819.161|819.316	873.023|871.064	2.132|2.117	31.667|30.356
		CI[1,c]	813.956|814.060	809.213|809.335	863.864|862.081	2.976|2.965	31.318|30.134
		ACPF-2[1,d]	821.605|821.728	818.569|818.731	872.832|873.010	1.905|1.881	32.145|32.180
		CI[1,d]	812.474|812.574	808.265|808.394	863.215|863.368	2.641|2.623	31.840|31.874
5202/2000 72/20	208|404	CASSCF	604.097|604.470	594.042|594.292	667.429|667.429	6.309|6.387	39.741|39.507
		ACPF-2[1,c]	825.493|825.577	822.973|823.089	876.395|876.440	1.581|1.561	31.942|31.917
		CI[1,c]	819.755|819.787	816.592|816.622	871.933|871.973	1.985|1.986	32.742|32.747
		CASSCF[e]	604.097|604.466	594.042|594.289	667.417|667.417	6.309|6.386	39.734|39.502
		ACPF-2[1,e]	825.493|825.573	822.972|823.085	876.377|876.422	1.582|1.561	31.930|31.908
		CI[1,e]	819.755|819.783	816.591|816.618	871.914|871.955	1.985|1.986	32.730|32.738
		ACPF-2[1,d]	825.343|825.411	822.876|822.969	876.853|876.981	1.548|1.532	32.323|32.361
		CI[1,d]	818.993|819.054	815.942|816.023	871.697|871.813	1.915|1.902	33.072|33.107
	148|285[d]	RASSCF	603.826|604.203	593.506|593.779	666.120|666.120	6.476|6.541	39.090|38.853
		ACPF-2[2,c]	825.447|825.536	822.913|822.913	876.352|876.399	1.590|1.646	31.943|31.917
		CI[2,c]	819.706|819.741	816.518|816.518	871.862|871.905	2.001|2.022	32.728|32.733
		RASSCF[e]	603.826|604.199	593.506|593.776	666.109|666.109	6.476|6.540	39.083|38.849
		ACPF-2[2,e]	825.446|825.531	822.913|823.033	876.334|876.381	1.589|1.568	31.933|31.909
		CI[2,e]	819.705|819.737	816.518|816.548	871.844|871.886	2.000|2.001	32.718|32.724
		ACPF-2[2,d]	825.274|825.345	822.799|822.898	876.810|876.947	1.553|1.536	32.339|32.381
		CI[2,d]	818.927|818.990	815.848|815.934	871.617|871.741	1.932|1.918	33.064|33.101
6202/2000 82/20	616|1204	CASSCF	622.054|622.320	610.676|610.891	672.996|672.996	7.140|7.172	31.966|31.800
		ACPF-2[1,c]	825.800|825.924	823.217|823.361	876.947|877.133	1.621|1.608	32.095|32.134
		CI[1,c]	821.006|821.074	817.768|817.830	872.810|872.979	2.032|2.036	32.508|32.571
		CASSCF[f]	622.047|622.047	610.663|610.663	672.918|672.918	7.144|7.144	31.922|31.922
		ACPF-2[1,f]	825.797|825.872	823.218|823.317	876.919|877.106	1.618|1.603	32.080|32.150
		CI[1,f]	821.004|821.071	817.765|817.852	872.772|872.942	2.033|2.020	32.485|32.550
		ACPF-2[1,d]	825.685|825.756	823.676|823.890	877.553|877.838	1.261|1.171	32.548|32.682
		CI[1,d]	820.880|820.944	817.604|817.795	872.994|873.252	2.056|1.976	32.702|32.824
	282|550	RASSCF	621.003|621.288	609.369|609.629	671.609|671.609	7.300|7.479	31.756|31.577
		ACPF-2[2,c]	825.699|825.826	823.106|823.248	876.852|877.042	1.627|1.618	32.099|32.139
		CI[2,c]	820.881|820.951	817.619|817.676	872.689|872.862	2.047|2.055	32.510|32.575
		RASSCF[f]	620.997|620.997	609.357|609.357	671.541|671.541	7.304|7.304	31.717|31.717
		ACPF-2[2,f]	825.695|825.768	823.106|823.193	876.823|877.016	1.625|1.616	32.083|32.159
		CI[2,f]	820.879|820.944	817.615|817.693	872.652|872.828	2.048|2.040	32.488|32.558

(*continued*)

TABLE I
(Continued)

AS	No. ref[a]	Method	F + H_2	Lin. TS. − (100. + x/1000)/E_h	FH + H	Lin. Barr.[b]	ΔE[b]
			$C_{2v}\|C_s$	$C_{2v}\|C_s$	$C_{2v}\|C_s$	$C_{2v}\|C_s$	$C_{2v}\|C_s$
		ACPF-2[2,d]	825.579|825.652	823.546|823.736	877.415|877.695	1.276|1.202	32.528|32.658
		CI[2,d]	820.748|820.813	817.445|817.616	872.826|873.081	2.073|2.006	32.679|32.799
7202/2000 92/20	1568|3080	CASSCF	629.493|629.758	618.351|618.351	680.432|685.286	6.992|7.158	31.965|34.844
		ACPF-2[1,c]	825.890|826.017	823.352|—	877.450|877.598	1.593|—	32.354|32.368
	462|903	RASSCF	628.100|628.386	616.601|616.601	678.895|683.676	7.216|7.395	31.874|42.091
		ACPF-2[2,c]	825.778|825.907	823.227|823.325	877.332|877.508	1.601|1.620	32.351|32.380
		CI[2,c]	821.520|821.592	818.378|818.465	873.572|873.880	1.972|1.962	32.663|32.811
		ACPF-2[2,d]	826.612|826.888	824.064|824.360	877.841|878.142	1.599|1.586	32.147|32.162
		CI[2,d]	821.795|822.046	818.594|818.860	873.572|873.846	2.009|1.999	32.491|32.505

* The 1σ orbital is frozen, and the 2σ orbital is inactive; [1] using CASSCF orbitals; [2] using RASSCF orbitals.

[a] Number of reference configurations in the $C_{2v}|C_s$ point groups.

[b] In kcal/mol^{-1}.

[c] All MCSCF orbitals were optimized for the same AS.

[d] The orbitals were optimized for the (7202/1000|92/10) AS.

[e] The 1σ orbit was taken from the (5101/2101|61/31) AS MCSCF calculation and frozen during the MCSCF calculation.

[f] The 1σ and 2σ orbitals were taken from the (5101/2101|61/31) AS MCSCF calculation and frozen during the MCSCF calculation.

radial correlation requires the inclusion of the F(3p) orbitals in the active space. This results in either the (5202/2000|72/20) AS, in which we make active the F(3p_x, 3p_y) orbitals or the (6202/2000|82/20) AS, in which the F(3p_z) orbital is also made active. As shown in Table I, the inclusion of the 3p_x and the 3p_y orbitals does not improve the artificial energy difference between C_s and C_{2v} symmetry. In fact, the energy difference in the MCSCF energies is more pronounced in the reactant asymptote (±400 μE_h) and at the linear transition state (±250 μE_h), but the ACPF-2 and CI energy artifacts decrease to just below 100 μE_h. In addition to the symmetry breaking just described, difficulties arose within the MCSCF orbital optimization process when using the (5202/2000|72/20) AS. In particular, it was difficult to retain the desired physical natures of the inactive and active orbitals.

In the 6202/2000 calculations, in the reactant asymptote we observed a strong competition for the 6σ orbital between F(3s) and F(3p_z). In the C_{2v} point group, we were able to keep the F(3p_z) orbital in the active space, but in the C_s calculations, the 8a' orbital involved a mixture of F(3s) and F(3p_z). This resulted in a lowering of the MCSCF energy in the C_s point group for the reaction asymptote. Also, when trying the (7202/2000|92/20) reference space at the reactant asymptote, where the F(1s) and F(2s) orbitals are inactive, while the H_2(1σ_g,1σ_u), F(2p), F(3p), and F(3s) orbitals are active, we found that the MCSCF optimization moved the H_2 2σ_g orbital into the active space in place of the F(3s) orbital. All these problems convinced us to consider the ASs in which only the F(1s) orbital is kept inactive.

Hence, in the second series of AS constructions (see Table II), only the (1σ/1a') orbital is kept inactive. For the (5202/1000|72/10) AS, the MCSCF optimization of all the orbitals leads to an undesired situation in which the H_2(σ_g) is the lowest (Fock) energy orbital and is thus inactive while the F(1s) orbital moves to be part of the active space along with the F(2s) F(2p_z), and the F(3s) orbitals. In the product asymptote, the orbital optimization for this choice of AS lowers the Fock energy of F(1s) thus making it inactive. The active orbitals in the product asymptote are the F(2s) orbital, the bonding and anti-bonding combination of the H(1s) and F(2p_z) and the distant H(1s) orbital as well as the F(2p_x, 3p_x, 2p_y, 3p_y) orbitals. Due to the unphysical composition of the active space in the reactant asymptote, we obtain extremely poor results for this AS. For example, in the CI and ACPF-2 calculations, the transition state barrier is absent (the barrier ob-

TABLE II

Energies of a F + H_2 system at the reactant, linear transition state, and product geometries, as well as the linear barrier height and the electronic exothermicity ΔE.*

AS	No. ref.[a]	Method	F + H_2	Lin. TS. − (100. + x/1000)/E_h	FH + H	Lin. Barr.[b]	ΔE[b]
			$C_{2v}\|C_s$	$C_{2v}\|C_s$	$C_{2v}\|C_s$	$C_{2v}\|C_s$	$C_{2v}\|C_s$
5202/1000 72/10	616|1204	CASSCF	619.137|619.137	603.533|603.533	669.028|669.028	9.792|9.792	31.307|31.307
		ACPF-2[1,c]	817.627|817.627	823.256|823.256	868.799|868.799	−3.532|−3.532	32.111|32.111
		CI[1,c]	814.160|814.160	815.800|815.800	864.908|864.908	−1.029|−1.029	31.845|31.845
		ACPF-2[1,d]	826.163|826.163	823.581|823.581	876.724|876.724	1.620|1.620	31.728|31.728
		CI[1,d]	819.751|819.751	816.759|816.759	872.256|872.257	1.878|1.878	32.947|32.948
		CASSCF[e]	617.896|617.896	603.497|603.497	668.753|668.753	9.035|9.035	31.914|31.914
		ACPF-2[1,e]	826.244|826.244	823.706|823.706	876.667|876.667	1.593|1.593	31.641|31.641
		CI[1,e]	820.149|820.149	816.184|816.184	872.257|872.258	2.488|2.488	32.698|32.699
5202/1000 72/10	376|725	ACPF-2[2,d]	826.077|826.084	823.488|823.498	876.666|876.677	1.625|1.623	31.745|31.748
		CI[2,d]	819.669|819.676	816.649|816.658	872.176|872.179	1.895|1.894	32.949|32.946
		RASSCF[e]	617.063|617.374	602.566|602.941	667.422|667.422	9.097|9.057	31.601|31.406
		ACPF-2[2,e]	826.216|826.233	823.660|823.688	876.612|876.619	1.604|1.597	31.624|31.618
		CI[2,e]	820.098|820.123	816.107|816.148	872.176|872.183	2.504|2.494	32.679|32.668
6202/1000	2308|4508	CASSCF	636.457|636.457	629.388|629.388	707.485|707.485	4.433|4.433	44.574|44.574
82/10	756|1464	RASSCF	635.262|635.262	627.419|627.419	704.062|704.062	4.921|4.921	43.173|43.173
		ACPF-2[2,c]	826.004|826.010	823.536|823.544	876.569|876.568	1.549|1.547	31.730|31.726
		CI[2,c]	821.698|821.703	818.834|818.840	873.679|873.679	1.797|1.797	32.619|32.615
		ACPF-2[2,d]	826.140|826.147	823.482|823.471	876.666|876.662	1.668|1.669	31.706|31.700
		CI[2,d]	821.333|821.338	818.391|818.396	873.778|873.777	1.846|1.846	32.910|32.906
		ACPF-2[2,f]	826.255|826.262	823.636|823.639	877.208|877.218	1.643|1.646	31.974|31.975
		CI[2,f]	821.464|821.470	818.274|818.277	873.198|873.207	2.002|2.004	32.464|32.465
7202/1000	7192|14112	CASSCF	659.844|659.844	649.667|649.667	715.790|715.790	6.386|6.386	35.107|35.107
		CASSCF[1,e]	659.830|659.830	649.655|649.655	715.774|715.774	6.385|6.385	35.106|35.106
	1276|2467	RASSCF[2,c]	657.086|657.086	646.519|646.519	712.152|712.152	6.630|6.630	34.554|34.554
		ACPF-2[2,c]	826.077|826.080	823.424|823.431	877.072|877.067	1.665|1.662	32.000|31.995
		RASSCF[2,e]	657.072|657.072	646.509|646.509	712.136|712.136	6.629|6.629	34.553|34.553
		ACPF-2[2,e]	826.199|826.202	823.525|823.530	877.046|877.042	1.678|1.677	31.907|31.903

* The 1σ orbital is frozen in all calculations; [1] using CASSCF orbitals; [2] using RASSCF orbitals.

[a] Number of references in the $C_{2v}|C_s$ point group.

[b] In kcal/mol^{-1}.

[c] All MCSCF orbitals were optimized for the same AS.

[d] The orbitals were optimized for the (7202/1000|92/10) AS.

[e] The 1σ orbital was taken from the (5101/2101|61/31) AS MCSCF calculation and frozen during the MCSCF calculation.

[f] The 1σ and 2σ orbitals were taken from the (5101/2101|61/31) AS MCSCF calculation and frozen during the MCSCF calculation.

tained with the ACPF-2 functional lies 3.532 kcal/mol^{-1} below the reactants.

The (6202/1000|82/10) active space differs from the preceding AS in the nature of its (1σ, 1a') orbital but encounters a similar problem as in the (6202/2000|82/20) AS calculation; that is, undesired swapping of the F(3p_z) and F(3s) orbitals in the reactant asymptote. However, use of the orbitals from the

(6202/2000|82/20) AS calculation in which the F(1*s*) and F(2*s*) orbitals are kept frozen while performing the (6202/1000|82/10) calculation remedies this problem. The subsequent ACPF-2 and CI energies differences between C_{2v} and C_s symmetries never exceeds 10 μE_h, which we view as tolerable (recall 0.1 kcal/mol^{-1} = 160 μE_h).

Finally, we investigated the (7202/1000|92/10) active space, in which the active orbitals are: F(2*s*), F(3*s*), F(2*p*), F(3*p*), $H_2(\sigma_g)$, and $H_2(\sigma_u)$, and the F(1*s*) orbital is inactive. In either the case where all orbitals are optimized in the MCSCF calculation, or where the lowest-lying orbital [i.e., F(1*s*)] is taken to be the lowest orbital of the (5202/1000|72/10) AS calculation, the MCSCF energies are identical in the C_{2v} and C_s point groups and the subsequent ACPF-2 and CI energies in the C_{2v} and the C_s point groups differ by <10 μE_h. So, we view either of these two AS strategies as potential candidates for use in our future explicitly correlated calculations.

Until now we only discussed using the CAS for each of the choices of reference space considered. We have also studied truncated versions of the aforementioned AS [the so-called restricted active spaces (RAS)] to reduce the number of configurations, without introducing significant symmetry breaking. In such studies we have a CAS but also allow for all singles and doubles from the orbitals that form the CAS into a secondary active space (cf. Ref. [59]). For the first series (Table I), the CAS contains all the active orbitals of the (5101/2000|61/20) AS and the secondary space consists of the other active orbitals of the AS which were not included in the CAS. The second series (Table II) differs from the first series by its CAS: (5101/1000|61/10) instead of the (5101/2000|61/20) CAS.

In summary, in the first series of AS constructions, only the smallest AS produces identical energies (MCSCF and CI) in C_{2v} and C_s symmetries for the same geometries. However, this small AS containing eight configurations is insufficient to study the complete PES due to the absence of a satisfactory description of the radial $2p \rightarrow 3p$ correlation, which is known to be essential. In all the other ASs of this series, the energies (e.g., as we observed in the CI-type calculations) obtained in the C_{2v} point group for the same geometries differ substantially from the energy obtained in the C_s point group. We therefore conclude that there is no active space of this type, where the two lowest orbitals are inactive, that is adequate for the F + H_2 reaction.

Among the second series of AS constructs, the orbitals from the (5202/1000|72/10) AS are unreliable, which results in an extremely poor description of the surface. This active space remains handicapped even when orbitals from the (7202/10|92/10) AS are used without reoptimization. The (6202/1000|82/10) AS using the orbitals from the (6202/2000|82/20) AS where the lowest two orbitals had been, in turn, taken either from the (5101/2101|61/31) AS or from the (7202/1000|92/10) AS are both good candidates for the final surface we are constructing. Finally, the (7202/1000|92/10) AS is also a good choice. Each of these latter ASs have negligible symmetry breaking (±10 μE_h). We also note (later) that the barrier heights and ΔE values obtained at the ACPF-2 level for any of these good ASs are very close to one another.

In a future article, we will report on the use of explicitly correlated methods using one or more of the above active spaces in an attempt to qualitatively improve upon the existing SW surface, generating a PES accurate to 0.1–0.2 kcal/mol^{-1}. In an earlier article [60], we investigated the HF molecule using the same explicitly correlated methods that we will apply to the F + H_2 PES, and we compiled a suitable atomic basis set containing 306 basis functions. The novelty of the r_{12} methods that we used resides in the fact that the computationally expensive three- and four-electron integrals can be avoided when the basis set is saturated up to 3*l* [70], where *l* is the orbital angular momentum quantum number of the outermost occupied shell (e.g., for F $l = 1$).

All of the above active spaces (e.g., 82/10 and 92/10) that qualify for an adequate description of the F + H_2 PES possess a large number of reference configurations (e.g., at least 1464 and 2467 references) that result in 437,890,804 and 709,739,204 configuration state functions when all single and double excitations are included and the $1a'$ orbital is correlated to generate the CI or ACPF wave function. A full-scale explicitly correlated calculation for the F + H_2 reaction that demands a rather large number of basis functions (to achieve at least the 3*l* saturation noted above) and more than 1,000 reference configurations (as in the acceptable ASs discussed above) is therefore beyond the actual scope of our present capability. Therefore, in generating the CI and ACPF-2 to use in our future r_{12} efforts, we plan to consider only those reference configurations that surpass a certain threshold (weight) in the nonexplicitly correlated ACPF-2 wave function. For this particular strategy, the 92/10 AS is more apt than the 82/10 AS. The 82/10 AS is affected by the undesired swapping of the F($3p_z$) and the F(3*s*)

TABLE III

Spectroscopic constants of the H_2 and the HF molecules and the reaction exothermicity (ΔE) for the $F + H_2$ reaction as calculated in this work and comparison with existing PES.

	H_2			HF			$F + H_2 \rightarrow FH + H$
	R_e/a_0	ω_e/cm^{-1}	D_e/kcal/mol^{-1}	R_e/a_0	ω_e/cm^{-1}	D_e/kcal/mol^{-1}	ΔE/kcal/mol^{-1}
This work	1.402	4456	109.00	1.735	4138	140.99	32.45[d]
SW [22]	1.400	4404	108.99	1.734	4131	140.32	31.77
ASW [46]	1.400	4413[e]	109.67[f]	—	—	—	31.34
Exp.	1.401[g]	4401[g]	109.53[g]	1.7328[h]	4138[i]	141.13[i]	32.002 ± 0.015[k]

[a] Interpol. to $V(R) = \sum \alpha_i/R^i$ (H_2: $R \equiv r_{HH'}$; HF: $R \equiv r_{FH}$), where $0 \leq i \leq 4$.

[b] H_2: $R/a_0 = \{1.38, 1.39, 1.40, 1.41, 1.42\}$.

[c] HF: $R/a_0 = \{1.71, 1.72, 1.73, 1.74, 1.75\}$.

[d] Calc. as $D_e(HF) - D_e(H_2) - (1/2)[\omega_e(HF) - \omega_e(H_2)]$.

[e] Fit to $E(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3$ (Table III in Ref. [46]).

[f] Calc. as $D_0 + E(v = 0)$ (Table III in Ref. [46]).

[g] Huber and Herzberg [72].

[h] Coxon and Ogilvie [73].

[i] Le Roy [74].

[j] Zemke et al. [75].

[k] Calc. as D_0(HF) [75] $-$ $D_0(H_2)$ [76].

orbital. The use of orbitals optimized in other AS [e.g., (6202|82/20) where the F(1*s*) and the F(2*s*) were kept frozen] can solve this deficiency (for the RAS and CAS AS). In case of reference selection we opted for the more secure path, i.e., the 92/10 AS where we are able to use the MCSCF orbitals optimized in the same AS.

4. Use of the New Active Space

In this section we describe how we used the (7202/10|92/10) reference space to characterize several chemically important loci on the $H_2 + F$ surface. All calculations are done in C_s symmetry, using the 92/10 AS, as this is the only symmetry that remains intact throughout the reaction. We employed the aug-cc-pVQZ basis set [64] and froze the core $1a'$ orbital in the ACPF-2 calculations as discussed in Section 2. We assessed the quality of our results by comparing them to results of the frequently used PES (SW and ASW) for this reaction and with the available experimental data.

4.1. DIATOMIC POTENTIALS AND EXOTHERMICITY OF THE F + H_2 REACTION

We first determined the nonrelativistic diatomic potential energy curves for H_2 and HF by fixing the F atom or one of the H atoms at a distance of 100 a_0, allowing us to generate the $F + H_2$ and $FH + H$ asymptotes of our PES. The equilibrium bond lengths R_e, harmonic frequencies ω_e and dissociation energies D_e for both diatomic molecules are given in Table III. We calculated R_e and ω_e by fitting the computed (92/10) ACPF-2 energies around R_e to a quartic polynomial in R^{-1}, where R is the interatomic distance, and finding the minimum and quadratic term in this function. The harmonic frequency was calculated using atomic masses instead of nuclear masses in order to simulate non Born–Oppenheimer effects [71].

The D_e result we obtained for H_2 is in close agreement with the value of Stark and Werner but is 0.67 kcal/mol^{-1} below the ASW result and is 0.53 kcal/mol^{-1} below the experimental finding. Our ω_e value deviates by 55 cm^{-1} from the experimental value and by a similar amount from the other theoretical results. We are convinced that the differences in ω_e are not due to our reference space, but inherent due to the size-extensivity errors for this particular geometry.

Our HF R_e, ω_e and D_e findings are in good agreement (e.g., 0.14 kcal/mol^{-1} for D_e) with the experimental results and a bit better than what the SW PES offers. However, although we slightly underestimate the dissociation energy (by 0.14 kcal/mol^{-1}), including the relativistic corrections does not help because our D_e is then reduced by 0.58

TABLE IV

Geometries and heights ($E^{\ddagger}$) of the constrained collinear and bent barriers calculated in this work and compared with existing PESs.

	Collinear barrier				Bent barrier			
	$r_{HH'}/a_0$	r_{FH}/a_0	$\theta/^{o}$	$E^{\ddagger\,a}$	$r_{HH'}/a_0$	r_{FH}/a_0	$\theta/^{o}$	$E^{\ddagger\,a}$
This work	1.441[b]	2.966[b]	0.00	1.666[b]	1.458[c]	2.923[c]	62.06[c]	1.318[c]
SW [22]	1.442	2.950	0.00	1.971	1.457	2.922	61	1.546
ASW [46]	1.442	2.936	0.00	1.92	1.457	2.916	64.5	1.53

[a] Barrier height in kcal/mol^{-1}.

[b] Fit to $V(x, y) = \sum \alpha_{ij} x^i y^j$ ($x \equiv r_{HH'}$; $y \equiv r_{FH}$) where $i + j \leq 2$. Grid: $x/a_0 = \{1.43, 1.44, 1.445, 1.45, 1.455\}$; $y/a_0 = \{2.83, 2.88, 2.93, 2.98, 3.03\}$.

[c] Fit to $V(x, y, z) = \sum \alpha_{ijk} x^i y^j z^k$ ($x \equiv r_{HH'}$; $y \equiv r_{FH}$; $z \equiv r_{FH'}$), where $i + j + k \leq 2$. Grid: $x/a_0 = \{1.45, 1.455, 1.46, 1.465\}$; $y/a_0 = \{2.88, 2.93, 2.98\}$; $\theta/^{o} = \{58, 61, 64, 67\}$.

kcal/mol^{-1} [60], thus moving it 0.72 kcal/mol^{-1} from the experimental findings.

Finally, our exothermicity is 0.45 kcal/mol^{-1} higher than the experimental value while the SW value is 0.23 kcal/mol^{-1} lower than the experimental result.

4.2. BARRIERS

The geometry and energy of the constrained linear barrier were determined by fitting our ACPF-2 computed energies to a quadratic polynomial in the interatomic distances r_{FH}, and $r_{HH'}$. The characteristics of the bent barrier were obtained by fitting our energies to a second-order polynomial in r_{FH}, $r_{HH'}$, and $r_{FH'}$. In both cases, the barrier was verified to have the curvatures appropriate to a transition state. The geometries for both barriers (Table IV) are in close agreement with the SW and ASW results, but our barrier heights are 0.25 to 0.30 kcal/mol^{-1} lower than those of SW or ASW. For the collinear barriers, our r_{FH} seems a little more elongated, and the angle θ for the bent barrier is closer to the SW value than to the ASW result.

4.3. VAN DER WAALS WELLS

The geometries of the van der Waals wells were obtained by fitting a grid of ACPF-2 computed energies to a second-order polynomial in the internal coordinates. For the (triangular) $F \cdots H_2$, we used the Jacobi-coordinates r($\equiv r_{HH'}$) and R as variables. For the (linear) $FH \cdots H$ well, we use the interatomic distances r_{FH}, and $r_{HH'}$. The results are represented in Table V. Our reactant well is a bit closer to the barrier than is the well on the SW or the ASW surface, and our well depth is deeper by 0.05 kcal/mol^{-1}. The geometry of our product well is slightly farther from the barrier than is the well on the SW surface and deeper by 0.06 kcal/mol^{-1}.

TABLE V

Geometries and depths (δE) of the van der Waals wells as calculated in this work and compared with existing PESs.

	$F \cdots H_2$				$FH \cdots H$			
	r/a_0	R/a_0	$\varphi/^{o}$	δE^{a}	$r_{HH'}/a_0$	r_{FH}/a_0	$\theta/^{o}$	δE^{a}
This work	1.404[b]	4.726[b]	90.00	0.413[b]	4.233[c]	1.737[c]	0.00	0.311[c]
SW [22]	1.40	4.771	90.00	0.350	4.19	1.74	0.00	0.25
ASW [46]	1.40	4.796	90.00	0.357	—	—	—	—

[a] Well depth in kcal/mol^{-1}.

[b] Fit to $V(x, y) = \sum \alpha_{ij} x^i y^j$ ($x \equiv r$; $y \equiv R$), where $i + j \leq 2$. Grid: $x/a_0 = \{1.395, 1.400, 1.405, 1.410\}$; $y/a_0 = \{4.65, 4.70, 4.75, 4.80\}$.

[c] Fit to $V(x, y) = \sum \alpha_{ij} x^i y^j$ ($x \equiv r_{HH'}$; $y \equiv r_{FH}$), where $i + j \leq 2$. Grid: $x/a_0 = \{4.200, 4.250, 4.300\}$; $y/a_0 = \{1.730, 1.735, 1.740\}$.

5. Conclusions

For many years, the F + H_2 reaction has been the subject of intense theoretical and experimental research in which significant progress has been achieved. For the time being, theorists are able to simulate the integral and differential cross sections, the reaction rate, and product HF vibrational-rotational state distribution in a quasi-quantitative way. However, even the newest generation of PESs has proved insufficiently accurate to obtain a higher level of agreement between the experimental data and the theoretical results. To reach this level, a new generation of PES for the F + H_2 reaction has to be constructed. As a first step toward this goal, we investigated the HF molecule earlier, using explicitly correlated methods in which we obtained nearly perfect agreement with the experimental data (R_e, ω_e, and D_e). In addition, we compiled and tested a basis set that can be used to calculate the F + H_2 PES, using explicitly correlated methods in a future effort.

In the present work, we carefully investigated the electronic configurations that can be used to calculate the new F + H_2 PES. We paid attention to the orbital composition of the AS along the reaction coordinate (in the reactant and product asymptotes and the transition state). We also monitored symmetry breaking, which was found to be so important that several ASs were incapable of describing the PES in a balanced way. Finally, we found that two ASs were suitable candidates to study the F + H_2 PES. The (6202/1000|82/10) AS and (7202/1000|92/10) ASs both have in common that only the lowest energy (in the MCSCF Fock matrix) molecular orbital (1*a*) remains inactive. However, both active spaces contain a large number (1464 and 2467, respectively) of reference configurations which, when single and double excitations are included in the CI and ACPF-2 wave functions, generate a huge number (up to 700 million) of configuration state functions. Because the r_{12} method requires rather large basis sets, the number of reference CSFs has to be reduced by selecting the most important. Among the two ASs mentioned, the (7202/1000|92/10) AS is the most appropriate to tackle the PES calculation because its molecular orbitals are not a compound of orbitals calculated in different active spaces.

In addition to identifying a set of ASs to use in our future explicitly correlated calculations, we used our new reference space (7202/1000|92/10) to calculate several important characteristics of the F + H_2 reaction using the nonexplicitly correlated ACPF-2 functional. We found that both van der Waals wells are slightly deeper than on the SW and ASW surfaces, the exothermicity is 0.45 kcal/mol^{-1} higher than the experimental findings, and the constrained linear and bent barriers are by ~0.3 kcal/mol^{-1} lower than that on the SW surface. Only the result for the harmonic frequency for the H_2 molecule is disappointing, which is not that much of a surprise due to the nature of the ACPF-2 functional.

Although deviations within the range of 0.3–1.0 kcal/mol^{-1} may seem small, they likely are behind the inability of even the SW/ASW surfaces to accurately reproduce experimental HF vibration-rotation state populations. In particular barrier height errors of ~0.25 kcal/mol^{-1} and exothermicity errors of ~0.45 kcal/mol^{-1} can cause difficulties. Therefore we will use the r_{12}-MR-ACPF-2 method to further improve the F + H_2 → FH + H PES.

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