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DISCLAIMER

THE H + $F_2 \longrightarrow$ HF + F REACTION.
AN AB INITIO POTENTIAL ENERGY SURFACE*

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ABSTRACT

Rigorous quantum mechanical calculations have been carried out to predict the H + $F_2 \longrightarrow$ HF + F potential energy surface. A double zeta basis set was used and open-shell self-consistent-field (SCF) calculations were carried out. In addition, electron correlation was explicitly treated using first order wave functions, made up of 553 $^2A'$ configurations. Orbitals were optimized by the interative natural orbital method. From the SCF calculations the barrier height and exothermicity are predicted to be 12.2 and 132.4 kcal/mole, respectively. The configuration interaction (CI) values are 1.0 and 88.3 kcal, in much better agreement with the experimental values, 1.2 and 102.5 kcal. The saddle point is predicted from the CI calculations to occur for a linear geometry, R(H-F) = 2.05Å, R(F-F) = 1.57Å. This corresponds to an H-F separation more than twice as great as in the HF molecule but an F-F separation is only slightly (0.03Å) longer than in the isolated F_2 molecule. A substantial number of calculations were carried out for nonlinear HF_2 to determine the anisotropy of the surface. Finally, a brief description is given of electronic structure changes during the reaction.

INTRODUCTION

Crossed molecular beam[1] and infrared chemiluminescence[2] experiments have been refined over the past fifteen years to the point where both methods are capable of yielding a truly impressive amount of information concerning the dynamics of chemical reactions. Perhaps the only family of reactions to which both methods have been successfully applied is the hydrogen atom plus halogen molecule family of exothermic reactions. The $H + C\ell_2$, $D + C\ell_2$, $H + Br_2$, and $H + C\ell I$ reactions have been studied by Polanyi and coworkers[3] using infrared chemiluminescence. For the $H + C\ell_2$ reaction, for example, they find that the ratio of product $HC\ell$ molecules found in the $v = 1, 2, 3$, and 4 vibrational levels is 0.32 to 0.67 to 1.0 to 0.21. McDonald, LeBreton, Lee, and Herschbach[4] have used crossed molecular beams to study the reactions $D + C\ell_2$, $D + Br_2$, $D + I_2$, $D + C\ell I$, and $D + BrI$. Herschbach and coworkers interpret the resulting angular distributions as indicating that although the reaction coordinate will be linear for the $D + C\ell_2$ reaction, it will be moderately bent for $D + Br_2$ and strongly bent for $D + I_2$.

The above experimental advances have generated an urgent need for a more adequate theoretical understanding of the dynamics of such simple reactions. In fact, the significance of the molecular beam prediction of a nonlinear reaction coordinate for $H + I_2$ in part derives from the fact that such behavior is not consistent with the London equation[5] (and its descendents[6]) for $A + BC$ potential energy surfaces. First principles theoretical studies of chemical reactions may be logically divided into two parts: a) the quantum mechanical calculation of the potential energy surface, and b) the calculation (given the potential surface determined above) of the reaction dynamics, which in a classical picture corresponds to the motion of the atoms on the potential surface. Although it is important to point out that very significant progress[7,8] is being made in the treatment of dynamics, our interest in the present paper is in part a) of the theoretical problem. Happily, the need for reliable a priori potential surfaces for systems of chemical interest is now beginning to be met. As well as the H_3 surface of Shavitt, Stevens, Karplus, and Minn,[9] and the H_3^+ surface of Csizmadia and coworkers,[10] a surface approaching quantitative accuracy for the $F + H_2 \longrightarrow FH + H$ reaction has recently been reported.[11] In the present work we present the preliminary results of a study which we hope will eventually yield a surface of chemical accuracy for the $H + F_2 \longrightarrow HF + H$ reaction.

From a theoretical point of view, it is clear that the $H + F_2$ surface (with only 19 electrons) is more amenable to a priori calculations than the other members of the $H + X_2$ family of potential surfaces. Further, the $H + F_2 \longrightarrow HF + F$ reaction may be the most interesting due to its extreme exothermicity,[12] 102.5 kcal/mole. However, from the experimental side, the $H + F_2$ reaction has been studied much less thoroughly than either $H + Cl_2$ or $H + Br_2$. No molecular beam experiments have been carried out on $H + F_2$, and only recently has a preliminary study[13] of the infrared chemiluminescence been reported. The chemiluminescence results indicate[13] that the $v = 5$ state of HF is the most populated. Only recently has an experimental value of the Arrhenius activation energy been reported,[14] 2.4 ± 0.2 kcal/mole. Despite the relatively limited amount of experimental data presently available concerning $H + F_2 \longrightarrow HF + H$, it is to be expected that this reaction will receive much attention in the future, in part because of its relation to the $H_2 - F_2$ laser.[15]

To conclude this introduction we note that Blais[16] has already reported a classical trajectory study of H + F_2, while Jaffe and Anderson[17] and Muckerman[18] have begun trajectory work on the same system. All three of these studies assume potential energy surfaces of the semi-empirical London-Eyring-Polanyi-Sato (LEPS) variety.[5,6,19] The work of Blais is consistent with the chemiluminescence experiments[13] in that he predicts HF to be formed preferentially in the v = 5 state.

THEORETICAL APPROACH

A double zeta basis set of contracted gaussian functions[20] was used in the present calculations. More specifically, the primitive gaussian basis sets of Huzinaga[21] (four s functions for H and nine s and five p functions for F) were contracted following Dunning[22] to two s functions for H and four s and two p functions for F. We designate[20] this basis H(4s/2s), F(9s5p/4s2p).

It is appropriate at this point to discuss how reliable calculations employing the above basis are likely to be. The best source of information of this type would appear to be our earlier calculations on F + H_2 $\longrightarrow$ FH + H. When configuration interaction (CI) calculations[11a] of the type to be described shortly were carried out for FH_2 with the above basis, a barrier height of 5.7 kcal and exothermicity of 20.4 kcal/mole were predicted. These quantities may be compared to the experimental activation energy, 1.7 kcal, and exothermicity, 31.8 kcal. These FH_2 results were deemed qualitatively reasonable as the reaction is properly predicted to have a low activation energy and substantial exothermicity. It was later found[11b] that the failings of the double zeta basis results were primarily due to the lack of polarization functions[20] (p functions on H and d functions on F). For FH_2, the addition of polarization functions to the basis yielded very good results, a barrier height of 1.66 kcal and exothermicity of 34.4 kcal. We conclude that, while the present double zeta basis leaves much to be desired, it is adequate for a first study of the $H + F_2 \longrightarrow HF + F$ potential surface.

One of the most surprising aspects of our $F + H_2$ study was how poorly the Hartree-Fock or self-consistent-field (SCF) approximation described the potential energy surface. Using the double zeta basis SCF calculations predicted a barrier height of 34.3 kcal/mole. When polarization functions were added, the result was still far too high, 29.3 kcal. Therefore it seems absolutely essential that electron correlation[20] be explicitly taken into account in the computation of repulsive[19] potential energy surfaces such as $F + H_2$ and (presumably) $H + F_2$.

As in our earlier work,[11] we have approached the correlation problem using multiconfiguration "first-order" wave functions. This type of CI wave function has been described adequately elsewhere,[23-27] and incorporates those correlation effects termed "internal," "semi-internal," and "polarization," by Silverstone and Sinanoglu.[28] When first-order wave functions are optimized by the interative natural orbital method,[29] they become rather similar to the "optimized valence configuration" wave functions of Wahl and Das.[30]

The selection of configurations for the HF_2 systems is quite straightforward, given the Hartree-Fock configuration for general geometry (C_s symmetry)

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 1a''^2\ 5a'^2\ 6a'^2\ 2a''^2\ 7a'^2\ 8a' \qquad (1)$$

For infinite $H - F_2$ separation, the first 9 orbitals in (1) correspond to the following F_2 orbitals:

$$1\sigma_g^{\,2}\ 1\sigma_u^{\,2}\ 2\sigma_g^{\,2}\ 2\sigma_u^{\,2}\ 1\pi_u^{\,4}\ 3\sigma_g^{\,2}\ 1\pi_g^{\,4} \qquad (2)$$

and the singly-occupied 8a' orbital is the hydrogen 1s orbital. The only valence orbital not occupied in the Hartree-Fock wave function is the 9a' orbital, which corresponds to the F_2 $3\sigma_u$ orbital at infinite H - F_2 separation. The first-order wave function for HF_2 then should include all configurations in which no more than one electron occupies an orbital beyond 9a'. However, in the present work we have limited the number of configurations by holding the inner eight electrons frozen in the HF_2 SCF orbitals, which are essentially the 1s and 2s orbitals of the F atoms. In addition, only a few triple excitations (configurations differing by three orbitals from the Hartree-Fock configuration) were included, while no quadruple excitations were included. Since only three valence spin orbitals are unoccupied in the SCF wave function, configurations differing by five or more orbitals from the Hartree-Fock will be rigorously excluded from the first-order wave function for HF_2. The types of configurations finally included are specified in Table I, yielding a total of 553 $^2A'$ configurations for HF_2. As in our earlier study[26] of NH_2, we have excluded doubly-excited $^2A'$ configurations i with zero matrix element H_{1i} with the SCF configuration.

Straight CI based on the SCF orbitals for HF_2 is unlikely to yield a potential surface of the desired accuracy. This is because the form of the 9a' orbital is of crucial importance to the efficacy of the first-order wave function. For separated H + F_2, the 9a' orbital should correlate the F_2 bond; for separated

HF + F, the 9a' orbital must correlate the HF bond. Near the saddle point the role of this first SCF-unoccupied orbital is even more crucial. It is fairly clear that the HF_2 virtual SCF orbital cannot fulfill these three roles.[20,31] In the present work we have optimized the 9a' orbital (and the other orbitals as well) by the iterative natural orbital method.[29] The entire CI calculation is repeated in terms of the natural orbitals[32] from the previous CI until the total energy differed by less than 0.0001 hartree from the previous iteration. Typically seven iterations were required, somewhat more than is usually the case.

We will describe the geometry of HF_2 in the coordinate system used earlier[11] for FH_2. That is, a single point on the surface is specified by the HF separation R(H-F), the FF separation R(F-F), and θ, the H-F-F angle. Most (about 150) of the present computations were carried out for linear HFF, in light of the assumed reaction coordinate.

Since relative energies only will be quoted in the rest of the paper, it is appropriate to indicate the total energies of separated H + F_2, -199.2055 (SCF) and -199.3266 (CI) and HF + F, -199.4164 (SCF) and -199.4674 (CI).

THE LINEAR SURFACE

Assuming the minimum energy path to occur for a linear H-F-F arrangement, a sufficient number of calculations were carried out to pin down the reaction coordinate. These calculations are summarized and compared with experimental data in Table II. The HF_2 results are consistent with those obtained for FH_2 in that the configuration interaction surface represents a great improvement over the SCF surface.

The SCF barrier height for H + F_2 is about 10 times larger than the "experimental" value of 1.2 kcal suggested by Muckerman's work. For F + H_2, of course, this discrepancy was even worse. Surprisingly, the barrier height predicted from the present CI calculations is in excellent agreement with experiment. The reason for our surprise was that the comparable calculation for FH_2 yielded a barrier height about three times larger than the experiment. Our second FH_2 paper, of course, showed that use of a basis set including fluorine d and hydrogen p functions yields an excellent barrier height. At any rate, the present barrier height results suggest that our double zeta basis, first order wave functions provide a better description of the H + F_2 reaction than the F + H_2 reaction.

The exothermicity of the H + F_2 ⟶ HF + F reaction is predicted to be 29.9 kcal too large from our SCF calculations, while for F + H_2 the analogous result was 31.8 kcal too <u>small</u>. Although the two errors are of the same absolute value, it does not appear that the SCF approximation will give consistent results for heats of reaction of exothermic reactions. The CI result for HF_2 is 14.2 kcal smaller than experiment, while for FH_2 the analogous result was also smaller, by 10.8 kcal in that case.

While the saddle point geometry is not obtainable from experiment, it is worthwhile comparing the present results with those for FH_2. In both calculations the primary effect of CI is to push the saddle point into the entry channel. For H + F_2 the HF distance at the saddle point increases by 0.49Å with CI. If the FH_2 results are indicative, then the extension of the basis will yield an even longer HF distance and shorter F-F distance for the true saddle point geometry. In general, of course, one expects[20] electron correlation to have relatively small effect on geometry predictions. The problem arising in the present type of calculation is that the potential surface is very flat near the saddle point and a relatively small change in the surface can shift the saddle point position radically.

Table III shows the minimum energy path predicted by the first order (CI) calculations. There we see that the saddle point does indeed occur quite "early," i.e. the F-F separation is only 0.055 bohrs = 0.03Å longer than the equilibrium separation in the isolated F_2 molecule. The H-F distance at the saddle point is more than twice that for isolated HF at equilibrium. The above saddle point geometry for $H + F_2 \longrightarrow HF + F$ is quite consistent with Hammond's idea[33] that in a highly exothermic reaction the transition state will closely resemble the reactants.

Also indicated in Table III is the minimum energy geometry for the long range attraction between H and F_2. We find only a very small attraction, 0.05 kcal/mole, in the entry channel. However, there is a much stronger attraction, 0.55 kcal, between HF and F. The latter attraction is strongest for HF at its equilibrium geometry and an F-F distance of 5.23 bohrs. Although the reliability of these long range attraction predictions is only ∿ 0.2 kcal, this is sufficient to rule out the existence of a sizeable (∿ 2 kcal) well in either the entry or exit channel.

Perhaps the most significant of the known errors in our $H + F_2$ potential surface is the poor prediction of the F-F equilibrium internuclear separation. As Table III shows the double zeta CI calculations predict R_e(F-F) to be 2.905 bohrs, while the experimental separation is 2.68 bohrs.[34] This unusually large error of 0.12Å is due to the small dissociation energy of F_2 and resulting relative flatness of the potential curve. Addition of d functions on F to our basis will undoubtedly[35] eliminate most of this error. We note that the predicted HF distance, 1.789 bohrs, is in much closer agreement with the experimental value,[36] 1.733 bohrs.

ANGULAR DEPENDENCE OF THE SURFACE

Table IV summarizes our calculations on nonlinear HF_2. The chosen four sets of HF and FF distances correspond to four points near the linear minimum energy path. Table IV indicates that both SCF and CI calculations predict the minimum energy path to be linear. This result is consistent with the LEPS model[5,6] and also with the experimental finding of McDonald et.al.[4] that the reaction coordinate is linear for $H + C\ell_2$, moderately bent for $H + Br_2$, and strongly bent for $H + I_2$. Near the saddle point, the interaction energy goes from 1.06 kcal at $\theta = 0°$ to 4.64 kcal at $\theta = 90°$. The increase of 3.58 kcal/mole on bending may be compared with the analogous result for $F + H_2$, 3.61 kcal/mole. Thus the anisotropies of the two surfaces are remarkably similar in the simplest picture. It should be pointed out that the barrier height for $H + F_2$ at $\theta = 90°$ will undoubtedly be greater than 4.64 kcal/mole, because the position of the saddle point shifts as θ is changed. In our preliminary $F + H_2$ surface[11a] the saddle point for $\theta = 0°$ was R(F-H) = 2.58, R(H-H) = 1.54 bohrs while for $\theta = 90°$ R(F-H) = 2.35 and R(H-H) = 1.87 bohrs. And for $F + H_2$, the barrier height increases from 5.72 kcal at $\theta = 0°$ to 17.52 kcal and $\theta = 90°$. If this trend is carried over to $H + F_2$ (we did not carry out enough nonlinear calculations to resolve this question), the barrier height for the 90° approach would be $\sim$ 13 kcal/mole.

ELECTRONIC STRUCTURE CONSIDERATIONS

A simple picture of the electronic structure changes which occur during the $H + F_2 \longrightarrow HF + F$ reaction would provide some insight into the nature of concerted reactions. Finding such a picture might appear difficult, especially when one is dealing with 555 configuration wave functions. However, natural orbital occupation numbers[37] provide just such a simple picture. For the reactants, saddle point, and products, the natural orbital occupation numbers are given in Table V. The 9a' occupation numbers provide the key to understanding the primary electronic structure change that occurs with the reaction. Starting with the reactants, the 9a' orbital is quite important when one realizes that this orbital is not occupied in the SCF wave function. For $H + F_2$, the 9a' orbital is just the antibonding $3\sigma_u$ orbital of F_2. At the saddle point, the 9a' orbital becomes even more important, having occupation number 0.1854. This is an indication that there is more correlation energy (11.2 kcal/mole in our calculations) at the saddle point than for the reactants. The 9a' occupation number is much smaller, 0.0253, for the products. For HF + F the 9a' orbital is the antibonding 4σ orbital of HF. The diminution of the 9a' occupation number illustrates a serious weakness of the Hartree-Fock approximation: the energetic favoring of HF over F_2 and resulting exaggeration of the exothermicity.

The four most important spatial configurations are shown in Table VI. Interestingly, the order of importance of these four orbital occupancies is the same for reactants, saddle point and products. However, for reactants and saddle point the $7a'^2 \longrightarrow 9a'^2$ configuration is extremely important, while for products this is not true. It is to be noted that both the SCF and second configuration are required to dissociate to SCF wave functions for the three atoms.

For the SCF wave functions, Mulliken population analyses were obtained for the reactants [H(1.00), F_a(9.00) , F_b(9.00)], saddle point [H(0.019), F_a(9.496), F_b(9.485)], and products [H(0.511), F_a(9.489), F_b(9.00)]. This picture suggests that the system is more ionic at the saddle point than elsewhere.

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FOOTNOTES AND REFERENCES

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Table I. Spatial configurations included in the first-order wave function for the $^2A'$ electronic ground state of HF_2. na' refers to the 10a', 11a', ... orbitals, while na" refers to the 3a", 4a", ... orbitals. The basis set used in the present calculations included 18a' and 4a" functions.

Hartree-Fock Configuration

$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 1a''^2\ 5a'^2\ 6a'^2\ 2a''^2\ 7a'^2\ 8a'$

Replacement Relative to Hartree-Fock

$1a', 2a', \ldots\ 7a' \longrightarrow 8a'$

$1a', 2a', \ldots\ 7a' \longrightarrow 9a', na'$

$8a' \longrightarrow 9a', na'$

$1a'', 2a'' \longrightarrow na''$

$5a'^2, 6a'^2, 7a'^2 \longrightarrow 8a'\ 9a', 9a'^2$

$5a'\ 6a', 5a'\ 7a', 6a'\ 7a' \longrightarrow 8a'\ 9a', 9a'^2$

$5a'\ 8a', 6a'\ 8a', 7a'\ 8a' \longrightarrow 9a'^2$

$1a''^2, 2a''^2 \longrightarrow 8a'\ 9a', 9a'^2$

$1a''\ 2a'' \longrightarrow 8a'\ 9a', 9a'^2$

$5a'^2, 6a'^2, 7a'^2 \longrightarrow 8a'\ na'$

$5a'^2, 6a'^2, 7a'^2 \longrightarrow 9a'\ na'$

$5a'\ 6a', 5a'\ 7a', 6a'\ 7a' \longrightarrow 8a'\ na'$

$5a'\ 6a', 5a'\ 7a', 6a'\ 7a' \longrightarrow 9a'\ na'$

$5a'\ 8a', 6a'\ 8a', 7a'\ 8a' \longrightarrow 9a'\ na'$

$1a''^2, 2a''^2 \longrightarrow 8a'\ na'$

$1a''^2, 2a''^2 \longrightarrow 9a'\ na'$

Table I. (Continued)

Replacement Relative to Hartree-Fock (Continued)

$1a'' \; 2a'' \longrightarrow 8a' \; na'$

$1a'' \; 2a'' \longrightarrow 9a' \; na'$

$5a' \; 1a'', \; 6a' \; 1a'', \; \ldots . \; 7a' \; 2a'' \longrightarrow 8a' \; na''$

$5a' \; 1a'', \; 6a' \; 1a'', \; \ldots . \; 7a' \; 2a'' \longrightarrow 9a \; na''$

$8a' \; 1a'', \; 8a' \; 2a'' \longrightarrow 9a' \; na''$

$5a'^{2} 6a', \; 5a'^{2} \; 7a', \; \ldots . \; 6a'^{2} \; 7a' \longrightarrow 8a' \; 9a'^{2}$

$5a' \; 6a' \; 7a' \longrightarrow 8a' \; 9a'^{2}$

$1a''^{2} \; 5a', \; 1a''^{2} \; 6a', \; \ldots . \; 2a''^{2} \; 7a' \longrightarrow 8a' \; 9a'^{2}$

$1a'' \; 2a'' \; 5a', \; \ldots . 1a'' \; 2a'' \; 7a' \longrightarrow 8a' \; 9a'^{2}$

Table II. Summary of self-consistent-field (SCF) and configuration interaction (CI) results for the H + F_2 reaction.

	SCF	CI	Experiment
Barrier Height (kcal/mole)	12.2	1.0	2.4 ± 0.2[a]
Exothermicity (kcal/mole)	132.4	88.3	102.5[b]
Saddle Point Geometry (Å)			
H-F	1.56	2.05	---
F-F	1.49	1.57	---

[a] Arrhenius activation energy, reference 14. Using transition state theory and an LEPS potential surface, Muckerman[18] has calculated the barrier height to be 1.2 kcal/mole less than the Arrhenius activation energy.

[b] Reference 12.

Table III. Minimum energy path for the H + F_2 —> HF + F reaction. Internuclear separations are given in bohrs and energies in kcal/mole relative to the reactants.

R (H-F)	R (F-F)	Energy	
10.0	2.905	0.00	Reactants
6.05	2.905	-0.05	Minimum
4.25	2.919	0.59	
4.0	2.940	0.95	
3.88	2.96	1.04	Saddle Point
3.5	2.988	0.85	
3.3	3.027	0.42	
3.1	3.119	-2.04	
2.9	3.245	-10.67	
2.7	3.357	-24.38	
2.5	3.448	-39.35	
2.3	3.522	-54.37	
2.1	3.598	-67.49	
1.9	3.651	-78.39	
1.789	4.0	-85.97	
1.789	5.23	-88.87	Minimum
1.789	10.0	-88.32	Products

Table IV. Summary of some calculations on nonlinear HF_2. The angle θ is defined in Fig. 1 of Ref. 11a. Energies are given in kcal/mole relative to separated H + F_2.

R(H-F)=4.25, R(F-F)=2.92

θ	SCF	CI
0°	9.35	0.55
10°	9.40	0.62
30°	9.78	0.97
50°	10.33	1.49
70°	10.77	1.92
90°	11.11	2.27

R(H-F)=3.00, R(F-F)=3.16

θ	SCF	CI
0°	-9.40	-5.72
10°	-9.32	-5.51
30°	-8.59	-4.49
50°	-7.15	-2.14
70°	-5.34	+0.00
90°	-2.78	+3.50

R(H-F)=3.87, R(F-F)=2.96

θ	SCF	CI
0°	12.37	1.06
10°	12.47	1.16
30°	13.20	1.90
50°	14.29	3.00
70°	15.20	3.94
90°	15.86	4.64

R(H-F)=2.75, R(F-F)=3.32

θ	SCF	CI
0°	-38.97	-21.70
10°	-38.91	-21.40
30°	-38.46	-21.31
50°	-37.57	-21.23
70°	-36.43	-20.86
90°	-34.55	-19.83

Table V. Natural orbital occupation numbers for three points on the $H + F_2 \longrightarrow HF + F$ potential energy surface.

	Reactants $H + F_2$	Saddle Point H-F-F	Products HF + F
1a'	2.0000	2.0000	2.0000
2a'	2.0000	2.0000	2.0000
3a'	2.0000	1.9999	1.9999
4a'	2.0000	1.9999	1.9996
5a'	1.9977	1.9976	1.9995
6a'	1.9905	1.9907	1.9945
7a'	1.8358	1.8223	1.9752
8a'	1.0000	1.0007	1.0002
9a'	0.1730	0.1854	0.0253
10a'	0.0052	0.0051	0.0051
11a'	0.0019	0.0021	0.0004
12a'	0.0004	0.0005	0.0003
13a'	a	0.0001	0.0002
14a'	a	a	a
15a'	a	a	a
16a'	a	a	a
17a'	a	a	a
18a'	a	a	a
1a"	1.9977	1.9976	1.9995
2a"	1.9905	1.9907	1.9946
3a"	0.0052	0.0051	0.0051
4a"	0.0019	0.0021	0.0003

[a] Occupation number less than 5×10^{-5}.

Table VI. Coefficients of the six most important configurations in the 555 configuration wave functions for H + F_2 ⟶ HF + F. Note[26] that for orbital occupancies 3. and 4., two linearly independent $^2A'$ configurations are included in the wave functions.

Orbital Occupancy	Reactants	Saddle Point	Products
1. SCF	0.9519	0.9464	0.9904
2. $7a'^2 \longrightarrow 9a'^2$	0.2738	0.2752	0.0852
3. $7a'\ 2a'' \longrightarrow 9a'\,3a''$	0.0706	0.0686	0.0709
	0.0145	0.0145	0.0110
4. $6a'\ 7a' \longrightarrow 9a'\ 10a'$	0.0539	0.0522	0.0559
	0.0478	0.0469	0.0450

FIGURE CAPTIONS

Fig. 1 Contour map of the linear HF_2 potential energy surface.

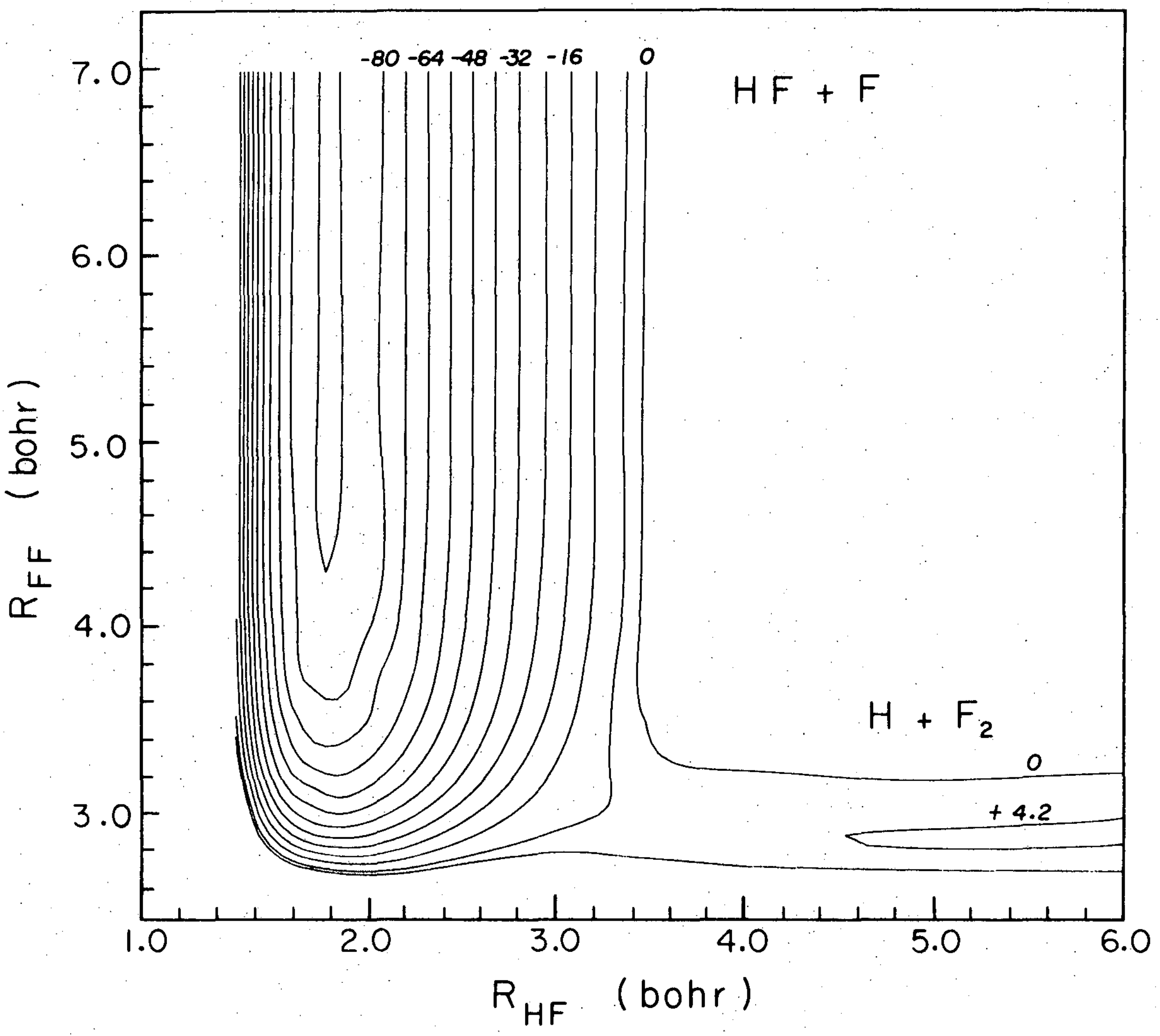

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Fig. 1

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