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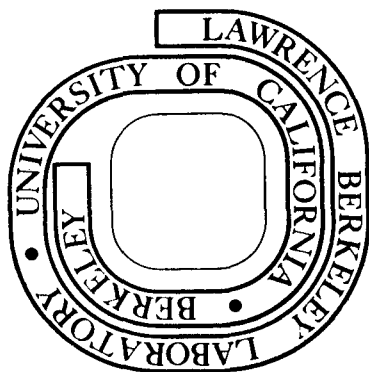
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POTENTIAL ENERGY SURFACES FOR FLUORINE HYDROGEN SYSTEMS

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Introduction

During the past decade, there has been a genuine explosion of interest in the reactions of atomic and molecular fluorine and hydrogen. As is usually the case, experimental studies have led the way, due in considerable measure to the tremendous impact of the HF laser. In addition to traditional kinetics (1), the most successful experimental techniques have been infrared chemiluminescence (2), chemical lasers (3), crossed molecular beams (4), and laser-induced fluorescence (5). This experimental research has yielded a great deal of important information concerning these elementary reactions. In addition, this work has stimulated a keen interest in the detailed understanding on the molecular level of how these simple reactions occur.

Given the above background, it is hardly surprising that there has been considerable theoretical activity directed toward fluorine hydrogen systems. From a theoretical viewpoint, the understanding of such reactions has two components: first, the potential energy surface (or surfaces) on which the pertinent reaction occurs, and secondly, the dynamics which occur given the potential surface(s). The amount of detailed experimental information now available for fluorine hydrogen reactions is sufficient to challenge the most sophisticated theorists of both the electronic structure and dynamics schools. Since dynamical considerations are taken up in a different chapter of the present volume, we will be concerned here with the potential surface half of the theoretical problem. Clearly, however, we must keep in mind the essential complementarity of these two pieces of the puzzle.

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**J. S. Guggenheim Fellow, 1976-1977.

In an interdisciplinary volume such as the present, it does not seem appropriate to give any sort of detailed coverage to the theoretical methods currently in use (6,7). It must be noted, however, that the Hartree-Fock or Self-Consistent-Field (SCF) method remains at the core of electronic structure theory. Although SCF theory is sometimes adequate in describing potential energy surfaces, this has turned out more often not to be the case. That is, electron correlation, which incorporates the instantaneous repulsions of pairs of electrons, can have a qualitative effect on the topology of fluorine hydrogen potential surfaces.

Without further introduction, it seems appropriate to proceed to a discussion of specific systems for which ab initio potential surface features have been predicted. In the present paper, special emphasis will be placed on the relationship between theoretical predictions and experimental observations.



Three progressively more reliable potential surfaces have been reported for this key reaction, which has become the focus of an enormous amount of scientific research. In the first (8), a double zeta (DZ) basis set was adopted. This notation implies that two basis functions are used to describe each orbital of the separated atoms. That is, for fluorine $1s$, $1s'$, $2s$, $2s'$, $2p_x$, $2p_x'$, $2p_y$, $2p_y'$, $2p_z$, and $2p_z'$ functions are adopted. Such a basis is clearly twice as large as the traditional minimum basis used in qualitative discussions of electronic structure.

Using the DZ basis and both SCF and configuration interaction (CI) methods, the results in Table I were obtained. It seems reasonable to conclude that the SCF results obtained with this basis are in poor agreement with experiment, while the CI results are much improved but even yet in only fair agreement. This conclusion was initially a surprise to us, since such techniques often yield rather reliable results, for example, in the prediction of equilibrium molecular structures (9).

The most obvious (in light of previous research (6,7) in this area) extension of the DZ basis is the addition of polarization functions, i.e., a set of d functions on fluorine and sets of p functions on each H atom. The basis thus obtained is labeled DZ + P and the ensuing results are summarized in Table I (10). There we see once again that the SCF approximation yields a barrier height much larger than experiment. And in fact even if one goes to a complete set of one-electron functions, the Hartree-Fock limit barrier height will be ~ 25 kcal larger than the true barrier. This inherent inability of the SCF approximation to even qualitatively describe repulsive potential surfaces must be viewed as one of the most important developments of our research to date.

Fortunately, the judicious use of CI yields a chemically reasonable DZ + P surface for $F + H_2$ (Figure 1). In particular, the predicted classical barrier height of 1.66 kcal is in fortuitously close agreement with the experimental activation energy. Further, the exothermicity of the BOPS surface is ~ 3 kcal greater than the experimental value. Thus, the primary significance of the BOPS CI surface was that it appeared to be the first qualitatively correct ab initio surface for a chemical reaction more complicated than the prototype (15) $H + H_2$ system.

The earliest indication of the qualitative correctness of the BOPS surface came from the classical trajectory studies of Muckerman (11). Muckerman varied several features of the London-Eyring-Polanyi-Sato (LEPS) surface for $F + H_2$ to get the best agreement between predicted and experimental (2,3) FH vibrational energy distributions. Although this work was done completely independent of the BOPS ab initio study, Muckerman's "best" semi-empirical surface (his surface V, summarized in Table I) has a saddle point position essentially indistinguishable from the BOPS surface. Since the saddle point position is probably the most critical surface feature not directly accessible to experimental determination, this concurrence was especially significant.

Perhaps the next important development was the fitting of the BOPS surface to an LEPS form by Polanyi and Schreiber (12). It should be noted that this fitting was carried out against the present authors' advice, our feeling being that the BOPS surface was not sufficiently accurate to be used without adjustment in dynamical studies. Nevertheless, Polanyi and Schreiber fit the 232 collinear points to the LEPS form with an ensuing rms deviation of less than 1 kcal per point. This exercise in itself is rather striking confirmation of the LEPS form, which has only seven adjustable parameters. The most obvious weakness of the BOPS-FIT surface was a spurious 0.4 kcal attractive well in the entrance valley. In addition, of course, the BOPS-FIT surface incorporated the known 3 kcal BOPS error in the predicted exothermicity.

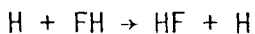
Collinear classical trajectory studies were then performed using the BOPS-FIT surface. By comparing with the experimental vibrational distribution, Polanyi and Schreiber (PS) concluded that although the BOPS surface was qualitatively reasonable, it does have a rather serious failing. That is, PS concluded that the BOPS surface drops too rapidly from the "shoulder" into the exit valley. It was noted, of course, that the known error of 3 kcal in the exothermicity is a major factor in this rapid drop. Our current feeling is that while this criticism of the BOPS surface may well prove to be at least partially valid, the use of classical (rather than quantum mechanical) dynamics and one (rather than three) dimension detracts from the strength of the PS conclusion.

Polanyi and Schreiber also suggested a "best" adjusted LEPS surface, their SE-I, and this surface is also summarized in Table I. There it is seen that the SE-I surface has its saddle point position somewhat later than either BOPS or Muckerman V. Nevertheless, it seems clear that the primary features of all three surfaces are rather similar. Both Muckerman (11) and Polanyi and Schreiber (12) have argued that the agreement between their best surfaces and the ab initio BOPS surface supports their use of the generalized LEPS form. We concur.

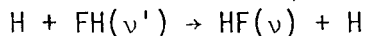
In an attempt to resolve some of the controversy arising from the BOPS surface, we decided in 1974 to attempt to determine an ab initio surface of sufficient reliability to be used directly or, with modest amounts of scaling, in dynamical studies. Recent developments (16) in the fully quantum mechanical treatment of A + BC reactions were another motivation for this research. However, one of us (CFB) discovered very quickly that apparent improvements in the quality of wavefunctions used led to a deterioration of the predicted FH₂ potential energy surface.

After an interval of contemplation, this research was continued in collaboration with Steven Ungemach and Bowen Liu (IBM, San Jose). Their conclusions have been presented (13) at the latest General Discussion of the Faraday Division of the Chemical Society (September 1976). Using a basis set more than twice as large as DZ + P and very large CI, USL predict a barrier of 3.3 kcal, with a suggested error of no more than one kcal. Thus, it now appears that the true barrier height is notably greater than the experimental activation energy. This idea is qualitatively supported by USL's additional prediction that there may be as much as 1.5 kcal less zero point vibrational energy at the saddle point than for separated F + H₂. Finally, it is worth noting that the USL saddle point geometry is about halfway between the Muckerman V-BOPS results and the PS SE-I prediction.

It should be clear from the above that the F + H₂ potential energy surface is likely to remain the source of much controversy for years to come. More generally, it seems apparent that the closer one looks at a particular problem, as both theoretical and experimental techniques become more sophisticated, the more fine structure comes to light.



As mentioned above, efforts to develop the HF chemical laser as a practical device have contributed greatly to the interest in elementary fluorine hydrogen systems. In this context, essentially every process leading to vibrational relaxation of HF must be precisely characterized. One of the simplest such processes



has been the subject of several studies, both experimental (5) and theoretical (17). Clearly, the barrier height or activation energy for this simple exchange reaction will play a critical role in the dynamics.

Since semi-empirical potential surfaces have been so successful in describing the $F + H_2$ dynamics, it is not completely unreasonable to assume that the same LEPS surfaces might be suitable for $H + FH$. After all, the latter reaction merely corresponds to a different channel of the FH_2 surface. And, in fact, this is precisely the procedure adopted by Thompson (17) and by Wilkins in their classical trajectory studies (18) of $H + FH$.

Table II summarizes the predictions of a number of semi-empirical FH_2 surfaces for the $H + FH$ barrier. The final entry indicates that rather reliable CI calculations (19), using a better than double zeta plus polarization basis set, predict a barrier of 49 kcal. BGS concluded in their paper (19) that the true collinear barrier is no less than 40 kcal. Thus, it is seen that the two "best" semi-empirical $F + H_2$ surfaces, Muckerman V and Polanyi-Schreiber SE-I, fail miserably for the collinear $H + FH$ channel. This is perhaps the strongest evidence to date for the importance of ab initio information in potential energy surface calibration.

Two very recent (yet unpublished) papers support the qualitative conclusions of BGS. Using a very large basis, Meyer (20) has predicted a collinear barrier of 45 kcal/mole for $H + FH \rightarrow HF + H$ using the coupled electron pair approximation. Attempts to estimate the true barrier via error analysis lead to a value of ~ 40 kcal. Secondly, Winter and Wadt (21) have found that the use of diffuse basis functions yields a surface which is quite "flat" with respect to the HFH bond angle. In fact, the true saddle point may occur for a bond angle less than 180° and yield a barrier as low as 35 kcal. However, this conclusion must be considered tentative at the present time.

The primary physical (or chemical, according to one's preference) conclusion is that at energies below 35 kcal the atom exchange mechanism cannot be a significant contributor to the vibrational relaxation of HF by hydrogen atoms. This conclusion seems to be given remarkable support by the recent experiments of Heidner (5). Specifically, he finds that the cross section for vibrational relaxation increases enormously between $v = 2$ and $v = 3$. It seems more than coincidental that the $v = 3$ state of HF has enough internal energy to surmount the hypothesized barrier of 35 kcal/mole.

$H + F_2$ and $F + HF$

Polanyi and coworkers (22) have made truly impressive infrared chemiluminescence studies of this highly exothermic reaction. They find that the ratios of populations of the HF product vibra-

tional states ($v = 1$ up to $v = 9$) are 12:13:25:35:78:100:40:26:
<16.

Electronic structure theory has been applied (23,24) in a manner analogous to the first four columns of Table I, and these results are summarized in Table III. A significant difference between these $H + F_2$ results and the earlier $F + H_2$ studies (8,10) is that the DZ CI barrier is lower than that obtained with the more reliable DZ + P CI. Since (for reasons discussed above) it is difficult to determine the true barrier, it must be concluded that both methods yield barriers roughly compatible with the experimental activation energy. However, the superiority of the DZ + P basis does become apparent with an inspection of the calculated exothermicities.

Both the $F + H_2$ and $H + F_2$ surfaces were found to be in harmony with the LEPS model in their angular characteristics. That is, the true saddle point does occur for a collinear geometrical arrangement. It is worth noting (8,23) that the two surfaces become repulsive at about the same rate. The angle of approach is bent away from 180° . For the $F + H_2$ system, e.g., it is found (8) that constraining the F-H-H angle to be 90° yields a barrier 11 kcal higher than that obtained for $\theta(F-H-H) = 180^\circ$.

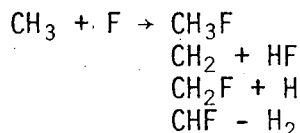
Another part of the HF_2 surface which has been carefully explored is the collinear $F + HF$ exchange reaction. This is another process of vital importance for an adequate understanding of the HF chemical laser. The results of OSB (25) are summarized in Table IV. There it is seen that the most reliable predicted barrier height is 24 kcal. On this basis, the true barrier was estimated to be ≥ 18 kcal. This result is much greater than the 6 kcal predicted (26) by the BEBO method. However, good agreement is found with Thompson's LEPS surface (27) calibrated for use on the $H + F_2$ reaction dynamics. The primary conclusion one can draw from these results is that the atom exchange mechanism is unlikely to contribute to the vibrational relaxation of the $v = 1$ state of HF. However, $v = 2$ relaxation could be greatly enhanced by atom exchange.

A final surface worth mentioning is that for the HF dimer. Among many theoretical studies, the most complete is that of Yarkony and coworkers (28). Although only the non-reactive part of the surface was considered, this portion is very relevant to the laser-related problems of rotational and vibrational energy transfer. The HF-HF surface has been fit to an analytical form by Alexander (29) and is being used in several dynamical studies in progress.

Concluding Remarks

It should be apparent that *ab initio* electronic structure theory is capable of genuine contributions to the understanding of simple fluorine atom reactions. This research is by no means a closed book, and an example from our current research should make

this clear. We have just begun the study of the $\text{CH}_3 + \text{F}$ radical reaction for which several products are possible:



This research is being done in conjunction with crossed molecular beam studies by Professor Y. T. Lee and should provide a rather detailed picture of this simple but multi-faceted reaction.

Abstract

Ab initio molecular electronic structure theory has now progressed to the point where it is capable of making genuine contributions to the understanding of simple chemical reactions. Especially noteworthy examples are the elementary fluorine hydrogen reactions pertinent to the HF chemical laser. The present paper discusses the reactions $\text{F} + \text{H}_2 \rightarrow \text{FH} + \text{H}$, $\text{H} + \text{FH} \rightarrow \text{HF} + \text{H}$, $\text{H} + \text{F}_2 \rightarrow \text{HF} + \text{H}$, and $\text{F} + \text{HF} \rightarrow \text{FH} + \text{F}$, with particular emphasis on the relationships between ab initio theory and experiment. Directions for future research are suggested.

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Table I. Some features of ab initio and semi-empirical potential energy surfaces for $F + H_2 \rightarrow FH + H$

Year	Surface	Saddle Point Geometry (angstroms)		Barrier Height (kcal/mole)	Exothermicity (kcal/mole)
		r (F-H)	r (H-H)		
1971	Double Zeta (DZ) Self-Consistent-Field (SCF) ^a	1.06	0.81	34.3	-0.6
1971	DZ Configuration Interaction (CI) ^a	1.37	0.81	5.7	20.4
1972	DZ + P SCF ^b	1.18	0.836	29.3	34.4
1972	DZ + P CI ^b	1.54	0.767	1.7	13.2
1972	Muckerman V ^c	1.54	0.76	1.1	31.8
1974	Polanyi-Schreiber SE-I ^d	1.43	0.777	2.2	31.0
1976	Large Basis ^e Extended CI	1.48	0.778	3.3	31.3
	Experiment	--	--	1.6 ^f	31.5 ± 0.5 ^g

^aReference 8

^bReference 10

^cReference 11

^dReference 12

^eReference 13

^fExperimental activation energy; see Reference 1

^gReference 14

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Table II. Barrier height and saddle point geometry for $\text{H} + \text{HF} \rightarrow \text{HF} + \text{H}$. The saddle point is assumed to occur for a linear symmetric H-F-H geometry.

Type of Potential Energy Surface	Authors	r (H-F), Å	Barrier (kcal/mole)
Bond-energy bond-order (BEBO)	Johnston ^a	1.10	6.8
London-Eyring-Polanyi-Sato (LEPS)	Muckerman I ^b	1.04	1.0
LEPS	Jaffe and Anderson ^c	1.04	-5.2
LEPS	Muckerman II ^b	1.04	1.0
	III	1.05	1.7
	IV	1.05	2.3
LEPS	Wilkins ^d	1.04	1.4
LEPS	Thompson ^e	1.12	28.6
Semi-empirical valence bond	Blais and Truhlar ^f	1.10	14.0
Diatomics-in-molecules	Tully I ^g	1.05	14.4
	II	1.09	13.1
LEPS	Muckerman V ^b	1.04	1.2
LEPS	Polanyi and Schreiber ^h	1.05	3.5
A priori methods			
Self-consistent field			
Configuration interaction	Bender, Garrison and Schaefer ⁱ	1.12	67.8
		1.14	49.0

^aJohnston, H. S., "Gas Phase Reaction Rate Theory" (Ronald, New York, 1966).

^bReference 11.

^cJaffe, R. L., Anderson, J. B., J. Chem. Phys. (1971), 54, (2224).

^dReference 18.

^eReference 17.

^fBlais, N. C., Truhlar, D. G., J. Chem. Phys. (1973), 58, (1090).

^gTully, J. C., J. Chem. Phys. (1973), 58, (1396).

^hReference 12.

ⁱReference 19.

Table III. Some features of *ab initio* potential surfaces (23,24) for $H + F_2 \rightarrow HF + F$

Surface	Saddle Point Geometry (angstroms)		Barrier Height (kcal)	Exothermicity (kcal)
	r (H-F)	r (F-F)		
DZ SCF	1.56	1.49	12.2	132.4
DZ CI	2.05	1.57	1.0	88.3
DZ + P SCF	1.61	1.41	13.9	130.1
DZ + P CI	1.68	1.50	4.1	99.0
Experiment	--	--	2.4 ± 0.2^a	102.5 ± 2.8^b

^aExperimental activation energy. Albright, R. G., Dodonov, A. F., Lavroskaya, G. K., Morosov, I. I., Tal'rose, V. L., J. Chem. Phys. (1969), 50, (3632).

^bDeCorpo, J. J., Steiger, R. P., Franklin, J. L., Margrave, J. L., J. Chem. Phys. (1970), 53, (936); Chupka, W. A., Berkowitz, J., J. Chem. Phys. (1971), 54, (5126).

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Table IV. Summary of theoretical potential energy surfaces (25) for the $F + HF \rightarrow FH + F$ exchange reaction.

Surface	Saddle Point Geometry r (HF), Å	Barrier Height (kcal/mole)
DZ SCF	1.087	53.8
DZ CI	1.126	21.8
DZ + P SCF	1.083	53.7
DZ + P CI	1.099	23.9

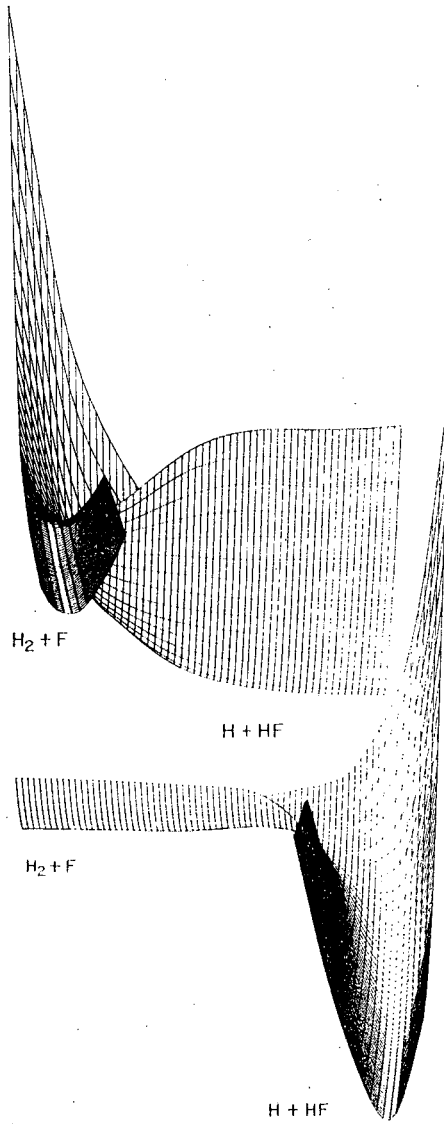


Figure 1

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