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A CRITICAL TEST OF SEMI-EMPIRICAL FH_2 POTENTIAL ENERGY SURFACES: THE BARRIER HEIGHT FOR H + FH → HF + H

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One of the fundamental goals of modern chemical physics is to determine the forces which govern atomic and molecular interactions. The most successful approach has traditionally been to work back from experimental observations to the hypothesized potential energy surface. This approach is perhaps best epitomized by the recent work of Lee, Barker, and colleagues,[1] in which experimental differential cross sections, second virial coefficients, and diffusion coefficients have been used to deduce interatomic potentials for noble gas pairs.

For polyatomic systems the procedures for deducing interaction potentials from experiment are at a much earlier stage of development. These procedures often rely heavily on data gleaned from infrared chemiluminescence,[2] chemical laser,[3] and crossed molecular beam[4] experiments. The system which has been studied most thoroughly to date is the $F + H_2 \rightarrow FH + H$ reaction. At least eleven semi-empirical potential energy surfaces have been proposed[5-13] for FH_2. Several[12,13] of these have been calibrated with experiment via an interative method, which begins with an assumed potential surface. Using this surface the dynamics are treated using classical trajectories and comparison made with experiment. Then the surface is adjusted and the process repeated until satisfactory agreement with the experimental findings is achieved.

Although most of the proposed FH_2 surfaces appear to reproduce the qualitative features of the vibrational energy distribution for $F + H_2 \rightarrow FH + H$, additional tests of these surfaces are needed before one can assume that a fundamentally correct description of

the interaction between these three atoms has been obtained. Although all of the semi-empirical surfaces yield essentially the correct barrier height (∿ activation energy) for the $F + H_2$ reaction, there is a second barrier height which any FH_2 potential should reproduce. This is the barrier for the exchange reaction $H + FH \rightarrow HF + H$. Furthermore, this barrier is of considerable importance in its own right, due to its role in the vibrational relaxation of HF by hydrogen atoms, a process which has already been the subject of two classical trajectory studies.[9,14]

The same sort of internal consistency test has already been completed for a related triatomic system, HF_2. There it has been found that two LEPS surfaces specifically tailored to describe $H + F_2 \rightarrow HF + F$ also yield reasonable values for the F + HF exchange reaction barrier.[15-18] The F + HF barriers of the Thompson[15] and Wilkens[16] surfaces are 27.8 and 22.4 kcal/mole, compared to theoretical results,[17] 21.8 and 23.9 kcal/mole. Thus there is ample reason to believe that semi-empirical surfaces for $F + H_2$ might do an adequate job of describing H + FH.

In the present paper, we report the H + FH barrier as obtained from a priori electronic structure theory. The theoretical method used was similar, but more exhaustive than that adopted in earlier studies[17,19,20] of $F + H_2$, $H + F_2$ and F + HF. A contracted gaussian basis set of size H(5s 1p/3s 1p), F(9s 5p 2d/5s 3p 1d) was employed. Thus we have added s and p functions on fluorine and an s function on hydrogen to the basis used in the study of the other fluorine-hydrogen systems. Furthermore, a more

complete configuration interaction (CI) was decided upon, including all interacting single and double excitations relative to the SCF or reference configuration. A total of 1583 configurations were included in the CI calculations.

The barrier occurs for a linear symmetric H-F-H structure, and our results are compared with the various semi-empirical surfaces in the Table. Although the a priori barrier height is likely to be somewhat higher than the exact (unknown) barrier, this difference is unlikely to be more than 5 kcal/mole. In any case we conclude that the true barrier height for H + FH is no less than 40 kcal/mole. As in previous studies of this type, we find electron correlation to be much more important (18.8 kcal/mole here) at the saddle point than for the reactants. The large barrier also rules out the possibility that F atom exchange is a significant contributor to the vibrational relaxation of HF by H atoms.

Most important, however, is the fact that all available semi-empirical potential surfaces for FH_2 fail to predict this large barrier for H + FH. Only Thompson's LEPS surface yields a qualitatively reasonable value for the barrier.[21] This of course does not necessarily mean that these surfaces are inappropriate for the study of the F + H_2 dynamics, for which most of them were designed. It does, however, raise serious questions about the fundamental ability of these semi-empirical forms to predict features of the true surface not known in advance.

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21. Note, however, that Thompson's surface predicts a barrier of 10.9 kcal/mole for $F + H_2 \rightarrow FH + H$.

TABLE. Barrier height and saddle point geometry for H + FH → HF + H. The saddle point occurs 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[5] I	1.04	1.0
LEPS	Jaffe and Anderson[6]	1.05	3.1
LEPS	Muckerman[7] II	1.04	1.0
	III	1.05	1.7
	IV	1.05	2.3
LEPS	Wilkins[8]	1.04	1.4
LEPS	Thompson[9]	1.12	28.6
Semi-Empirical Valence Bond	Blais and Truhlar[10]	1.10	14.0
Diatomics-in-Molecules	Tully[11] I	1.05	14.4
	II	1.09	13.1
LEPS	Muckerman[12] V	1.04	1.2
LEPS	Polanyi and Schreiber[13]	1.05	3.5
A Priori Methods	This work		
Self-Consistent-Field		1.12	67.8
Configuration Interaction		1.14	49.0

[a] H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald Press, New York, 1966).

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