A critical test of semiempirical FH_2 potential energy sufaces: The barrier height for H + FH → HF + H

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(Received 15 November 1974)

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 $F + H_2 - FH + H$ reaction. At least eleven semiempirical potential energy surfaces have been proposed[5-13] for FH_2. Several[12,13] of these have been calibrated with experiment via an iterative 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

TABLE I. Barrier height and saddle point geometry for H + HF → 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]	1.04	−5.2
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
Semiempirical 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, New York, 1966).

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 semiempirical 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, owing 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 semiempirical 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(5*s* 1*p*/3*s* 1*p*), F(9*s* 5*p* 2*d*/5*s* 3*p* 1*d*) 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 semiempirical surfaces in Table I. 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 semiempirical 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 semiempirical forms to predict features of the true surface not known in advance.

*Work performed under the auspices of the U. S. Atomic Energy Commission.
†Research supported by the National Science Foundation, Grants GP-39317 and 41509X.

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