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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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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 hy-
pothesized 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 develop-
ment.  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 experi-
mental 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 ($\sim$ 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 theo-

retical 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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     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).