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Authors
Bender, Charles F.
Garrison, Barbara J.
Schaefer, Henry P.

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Charles F. Bender, Barbara J. Garrison, and Henry F. Schaefer III

November, 1974

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A CRITICAL TEST OF SEMI-EMPIRICAL FH$_2$ POTENTIAL ENERGY SURFACES:

THE BARRIER HEIGHT FOR H + FH → HF + H

Charles F. Bender
Lawrence Livermore Laboratory*
University of California
Livermore, California 94550

and

Barbara J. Garrison and Henry F. Schaefer III
Department of Chemistry** and Lawrence Berkeley Laboratory*
University of California, Berkeley, California 94720

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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, 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, chemical laser, and crossed molecular beam experiments. The system which has been studied most thoroughly to date is the $\text{F} + \text{H}_2 \rightarrow \text{FH} + \text{H}$ reaction. At least eleven semi-empirical potential energy surfaces have been proposed for $\text{FH}_2$. Several of these have been calibrated with experiment via an interactive 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 $\text{FH}_2$ surfaces appear to reproduce the qualitative features of the vibrational energy distribution for $\text{F} + \text{H}_2 \rightarrow \text{FH} + \text{H}$, 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 \( \text{F} + \text{H}_2 \) reaction, there is a second barrier height which any \( \text{FH}_2 \) potential should reproduce. This is the barrier for the exchange reaction \( \text{H} + \text{FH} \rightarrow \text{HF} + \text{H} \). 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, \( \text{HF}_2 \). There it has been found that two LEPS surfaces specifically tailored to describe \( \text{H} + \text{F}_2 \rightarrow \text{HF} + \text{F} \) also yield reasonable values for the \( \text{F} + \text{HF} \) exchange reaction barrier.\(^{15-18}\) The \( \text{F} + \text{HF} \) 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 \( \text{F} + \text{H}_2 \) might do an adequate job of describing \( \text{H} + \text{FH} \).

In the present paper, we report the \( \text{H} + \text{FH} \) 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 \( \text{F} + \text{H}_2 \), \( \text{H} + \text{F}_2 \) and \( \text{F} + \text{HF} \). A contracted gaussian basis set of size \( \text{H}(5s\ 1p/3s\ 1p), \text{F}(9s\ 5p\ 2d/5s\ 3p\ 1d) \) 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 FH₂ fail to predict this large barrier for H + FH. Only Thompson's LEPS surface yields a qualitatively reasonable value for the barrier. This of course does not necessarily mean that these surfaces are inappropriate for the study of the F + H₂ 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.
References


12. J. T. Muckerman, unpublished "Surface V" for the FH\textsubscript{2} system. Despite the fact that this surface has not been published, it has been used in a number of dynamical studies. E.g., G. C. Schatz, J. M. Bowman, and A. Kuppermann, J. Chem. Phys. 58, 4023 (1973).


21. Note, however, that Thompson's surface predicts a barrier of 10.9 kcal/mole for F + H$_2$ → FH + H.
TABLE. Barrier height and saddle point geometry for $H + FH \rightarrow HF + H$. The saddle point occurs for a linear symmetric H-F-H geometry.

<table>
<thead>
<tr>
<th>Type of Potential Energy Surface</th>
<th>Authors</th>
<th>$r(H-F)$, Å</th>
<th>Barrier (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond-Energy Bond-Order (BEBO)</td>
<td>Johnston\textsuperscript{a}</td>
<td>1.10</td>
<td>6.8</td>
</tr>
<tr>
<td>London-Eyring-Polanyi-Sato (LEPS)</td>
<td>Muckerman\textsuperscript{5}</td>
<td>1.04</td>
<td>1.0</td>
</tr>
<tr>
<td>LEPS</td>
<td>Jaffe and Anderson\textsuperscript{6}</td>
<td>1.05</td>
<td>3.1</td>
</tr>
<tr>
<td>LEPS</td>
<td>Muckerman\textsuperscript{7}</td>
<td>1.04</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1.05</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>1.05</td>
<td>2.3</td>
</tr>
<tr>
<td>LEPS</td>
<td>Wilkins\textsuperscript{8}</td>
<td>1.04</td>
<td>1.4</td>
</tr>
<tr>
<td>LEPS</td>
<td>Thompson\textsuperscript{9}</td>
<td>1.12</td>
<td>28.6</td>
</tr>
<tr>
<td>Semi-Empirical Valence Bond</td>
<td>Blais and Truhlar\textsuperscript{10}</td>
<td>1.10</td>
<td>14.0</td>
</tr>
<tr>
<td>Diatomics-in-Molecules</td>
<td>Tully\textsuperscript{11}</td>
<td>1.05</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1.09</td>
<td>13.1</td>
</tr>
<tr>
<td>LEPS</td>
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<td>1.04</td>
<td>1.2</td>
</tr>
<tr>
<td>LEPS</td>
<td>Polanyi and Schreiber\textsuperscript{13}</td>
<td>1.05</td>
<td>3.5</td>
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<tr>
<td>\textit{A Priori} Methods</td>
<td>This work</td>
<td></td>
<td></td>
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<tr>
<td>Self-Consistent-Field</td>
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<td>1.12</td>
<td>67.8</td>
</tr>
<tr>
<td>Configuration Interaction</td>
<td></td>
<td>1.14</td>
<td>49.0</td>
</tr>
</tbody>
</table>

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