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and Charles F. Bender

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BARRIER HEIGHT FOR THE EXCHANGE REACTION F + HF ⟶ FH + F*

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The two classic systems for the study of reactive quantum mechanical tunneling are[1-3]

$$H + H_2 \longrightarrow H_2 + H$$

and

$$H + CH_4 \longrightarrow H_2 + CH_3$$

The merits of these two systems with respect to tunneling are at least three: a) both are relatively simple reactions, b) both have relatively high barrier heights (∿ 10 kcal), and c) both involve the transfer of the lightest atom, hydrogen. Thus $H + H_2$ and $H + CH_4$ are amenable to detailed calculation, and at thermal energies tunneling should contribute a significant fraction of the reactive cross sections.

A related system which might be considered a candidate for reactive tunneling is the

$F + HF \longrightarrow FH + F$ reaction.

Although the experimental activation energy is not known for the above reaction, in recent years it has been assumed[1] to be low, no more than 6 kcal. There are two reasons for this assumption. The first is Johnston's bond energy bond order (BEBO) method, which predicts the 6 kcal barrier. As ab initio theorists, we tend to be skeptical of empirical schemes such as BEBO. However, Truhlar[4] has recently shown that BEBO is remarkably accurate for the $H + H_2$ and $F + H_2$ reactions. Not only does BEBO accurately reproduce the activation energies, but it also predicts minimum energy paths within 0.03Å of those obtained from the most elaborate available ab initio calculations.[5,6] Thus the BEBO method for these two systems is far more accurate than could have been anticipated, and one should consider seriously the 6 kcal prediction for F + HF.

The second indirect piece of evidence against the existence of a substantial barrier for F + HF is the report by Pimentel and coworkers[7] of the observation of the linear molecules ClHCl, BrHBr, and IHI in noble gas matrices. By analogy with H_3, FH_2, and the general London-Eyring-Polanyi-Sato[8] (LEPS) view of potential surfaces, the saddle point for the X + HX exchange reactions should also occur for the linear symmetric ($D_{\infty h}$) XHX configuration. Thus the work of Pimentel suggests that for Cl + HCl, Br + HBr, and I + HI, there should be no barrier at all. This prediction is in turn not consistent with the kinetic studies of Klein, Persky, and Weston,[9] who found (by somewhat unconventional means) the barrier for Cl + HCl exchange to be $\sim$ 10 kcal. In

addition, Milligan and Jacox[10] have challenged the conclusions of Pimentel, voicing their opinion that the matrix isolated species are in reality $ClHCl^-$, $BrHBr^-$, and IHI^-. Very recently however, Pimentel's conclusions have been supported by the BEBO calculations of Truhlar, Olson, and Parr.[11] In addition to predicting ClHCl, BrHBr, and IHI to be bound by 1.56, 3.02, and 6.77 kcal, Truhlar et al. find vibrational frequencies in reasonable agreement with Pimentel's experimental values.

In the present communication we report ab initio calculations on linear symmetric FHF. Since the minimum energy path must pass through at least one geometry at which the two HF bond distances are equal, the lowest energy of symmetric FHF provides a lower limit to the barrier height for $F + HF \longrightarrow FH + F$.

Two basis sets of contracted gaussian functions[12] have been used in the present work. The first, a double zeta (DZ) set, is designated F(9s5p/4s2p), H(4s/2s). This is the same basis used in our previous calculations[13,14] of the $F + H_2$ and $H + F_2$ surfaces. The second basis, termed double zeta plus polarization (DZ + P), is described by the notation F(9s5pld/4s2pld), H(4slp/2slp). This second basis set yielded a surface[6] approaching quantitative accuracy for $F + H_2$.

Electron correlation was explicitly taken into account using multiconfiguration first order wave functions.[15] The form of this type of wave function is determined by symmetry considerations. Since F + HF refers to the same molecule as $H + F_2$, the reader is referred to our work[14] on $H + F_2$ for the list of configurations actually included. For linear FHF the first-order wave function constructed from the DZ + P basis includes 670 configurations. The orbitals of the multiconfiguration wave functions were optimized by the iterative natural orbital method.[16]

11. D. G. Truhlar, P. C. Olson, and C. A. Parr, J. Chem. Phys. 57, 4479 (1972).

12. T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).

13. C. F. Bender, P. K. Pearson, S. V. O'Neil, and H. F. Schaefer, J. Chem. Phys. 56, 4626 (1972).

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15. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results (Addison Wesley, Reading, Massachusetts, 1972).

16. C. F. Bender and E. R. Davidson, J. Phys. Chem. 70, 2675 (1966).

17. In discussing our result with colleagues, the only indirect support we have been able to locate comes from the semi-empirical LEPS potential surface used by N. Blais for his classical trajectory study of the H + F_2 reaction (Los Alamos Scientific Laboratories Report LA-4687). Blais found good agreement with experiment for the distribution of product vibrational energy. After concluding our study, we asked Dr. Donald L. Thompson of Los Alamos to obtain the F + HF ⟶ FH + F barrier from Blais's surface. The barrier height found was $\sim$25 kcal, in good agreement with the values reported here.

Table. Predicted barrier heights for F + HF ⟶ FH + F. See text for a brief description of the different wave functions.

Wave Function \ Property	r(H-F), Å	Barrier, kcal	Total energy, hartrees
DZ SCF	1.087	53.8	-199.3307
DZ CI	1.126	21.8	-199.4327
DZ+P SCF	1.083	53.7	-199.3578
DZ+P CI	1.099	23.9	-199.4676

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