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SOME FEATURES OF THE POTENTIAL ENERGY SURFACES FOR THE $F^+ + H_2$ ION-MOLECULE REACTION

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Some Features of the Potential Energy Surfaces

for the F^+ + H_2 Ion-Molecule Reaction[*]

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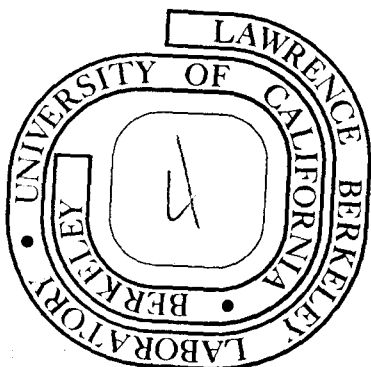
During the past five years, molecular beam[1-3] and theoretical[4-6] studies have yielded a great deal of important information concerning the dynamics of the $C^+ + H_2$ and $N^+ + H_2$ ion-molecule reactions. These systems are in some ways more interesting than typical neutral reactions, which can often be understood in terms of a single potential energy surface. At low energies both the C^+ and N^+ reactions with molecular hydrogen can be largely explained in terms of C_{2v} or near-C_{2v} orientations of approach.[5,6] The reagents may approach each other on a potential surface ($^2B_2$ for CH_2^+ and $^3A_2$ for NH_2^+) which is significantly attractive (e.g., $D_e(N^+-H_2) \sim 60$ kcal).[6] This surface is in turn connected to the ground state surface ($^2A_1$ for CH_2^+ and $^3B_1$ for NH_2^+) when the approaching heavy ion is moved off the H_2 perpendicular bisector, lowering the symmetry to C_s. The resulting complex formation[1,2] leads to products $CH^+ + H$ or $NH^+ + H$.

In the present note we present comparable theoretical results for the $F^+ + H_2$ system.[7] On first glance this reaction might appear quite analogous to $N^+ + H_2$ since F^+ with four 2p electrons is related to N^+ (two 2p electrons) in its particle-hole equivalence. However, there are some equally obvious differences between the $F^+ + H_2$ and $N^+ + H_2$ systems. For example, $N^+ + H_2$ is the energetic ground state of the separated system while $F^+ + H_2$ actually lies 46 kcal above $F + H_2^+$. Furthermore, even in combination with a reasonable understanding of the C^+ and N^+ reactions, a correlation diagram[8] (see Figure 1) for the $F^+ + H_2$ system does not make the route to the observed[7,8] products $HF^+ + H$ apparent.

As in Pearson's work[5] on $C^+ + H_2$ and ours[6] on $N^+ + N_2$, a double
zeta plus polarization basis set was adopted in conjunction with
configuration interaction (CI). The CI included all singly- and doubly-
excited configurations relative to one or two reference configurations.
Thus it seems reasonable to expect the present theoretical results to
be qualitatively valid.[9]

In Figure 2 we present the triplet part of a "vertical" ab initio
analogue to the empirical correlation diagram seen in Figure 1. The
C_{2v} results were obtained at r_e(F-H) = 0.963 Å, θ_e(HFH) = 112.1°,
the CI equilibrium geometry of the ground state $^1A_1$ FH_2^+ ion, and the
$D_{\infty h}$ results at r_e(F-H) = 0.959 Å, the lowest point on the linear
symmetric HFH^+ potential surface. It is apparent that all the excited
states of the FH_2^+ system lie very high in relative energy near the
ground state equilibrium geometry. We must conclude that the important
features of the FH_2^+ potential surfaces occur much "earlier" in the
approach of F to H_2^+ or of F^+ to H_2.

The critical region of configuration space for the C_{2v} $F^+ - H_2$
surfaces is clearly that "adjacent to" the reactants. This region
is seen in Figure 3, which illustrates the approaches of F to H_2^+ and
of F^+ to H_2. We were initially surprised[10] to find that the $^3A_2$ state,
which is so strongly bound[6] for $N^+ - H_2$, has only relatively weak long-
range attractive character for $F^+ - H_2$. Specifically, we find a
potential minimum of only ∿ 0.8 kcal, occurring at r(F-H) = 2.9 Å,

θ(HFH) = 15°. As predicted in Figure 1, the $^3B_1$ and $^3B_2$ states are even less attractive. Thus it would appear that C_{2v} or near C_{2v} approaches of F^+ to H_2 cannot possibly lead to reaction. This certainly confirms the conclusion[7,8] that $F^+ + H_2$ is a completely different kind of reaction than $N^+ + H_2$.

Turning to the surfaces arising from $F + H_2^+$, Figure 3 makes apparent the very strongly attractive character of the $^1A_1$ ground state. More interesting, in the present context, are the three triplet states, which have the same spin as the separated $F^+(^3P_g) + H_2$. As predicted in Figure 1, $^3B_1$ is the lowest of these, with an equilibrium geometry of r_e(F-H) = 1.67 Å, θ_e(HFH) = 31.6°, corresponding to an $F^+ - H_2$ dissociation energy of 17.5 kcal. The $^3B_2$ and $^3A_1$ states are reversed from the empirical correlation diagram, the $^3B_2$ being significantly bound, by 14.5 kcal, with its potential minimum at r_e(F-H) = 1.72 Å, θ_e(HFH) = 30.3°.

The possible significance of the $^3B_1$ and $^3B_2$ minima lies in the fact that the ground state $^1A_1$ surface can lead only to HF + H^+ products, i.e., not to $HF^+ + H$, the products observed experimentally.[7,8] It is not inconceivable that a suitable C_s distortion of these two minima might lead to products $HF^+ + H$ without a noticeable barrier. However, it is at least equally likely that there is a low energy pathway to HF^+ associated with $C_{\infty v}$ or near $C_{\infty v}$ approaches (F-H-H)$^+$.
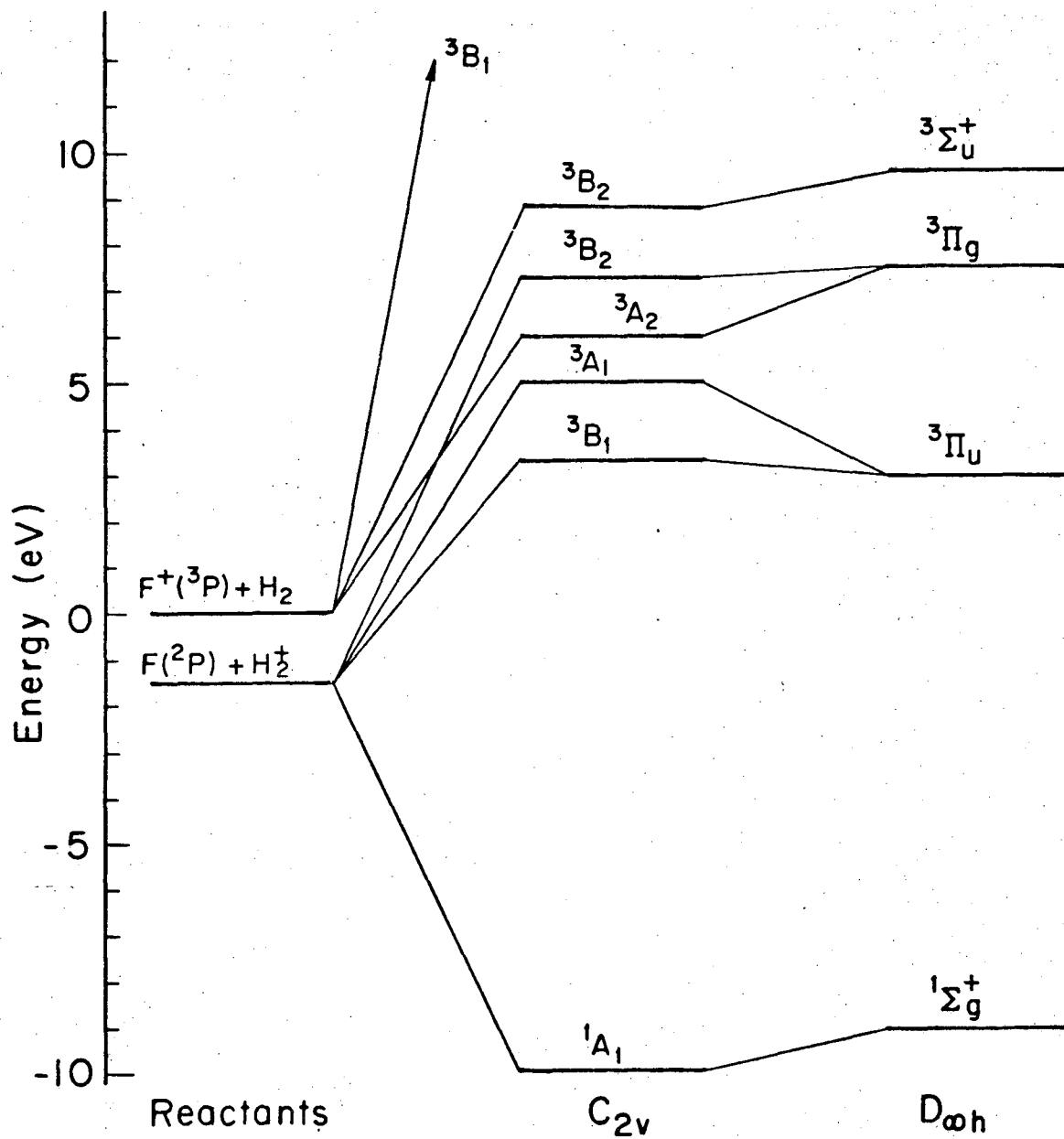
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8. This correlation diagram was constructed prior to the ab initio calculations reported here, to aid in the interpretation of molecular beam studies by S. G. Hanson and B. H. Mahan, unpublished.

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10. In retrospect, however, it is clear that the origin of the small bond angle states of CH_2^+, NH_2^+, and OH_2^+ is related (in the sense of Walsh's rules) to their singly-occupied $1b_2$ orbital. However, for FH_2^+, the dominance of the singly-occupied $1b_2$ orbital is countered by the energetically unfavorable $4a_1$ orbital, not occupied in OH_2^+.

Figure Captions

Figure 1. Empirical correlation diagram for the $(F^+ + H_2, F + H_2^+)$ system.
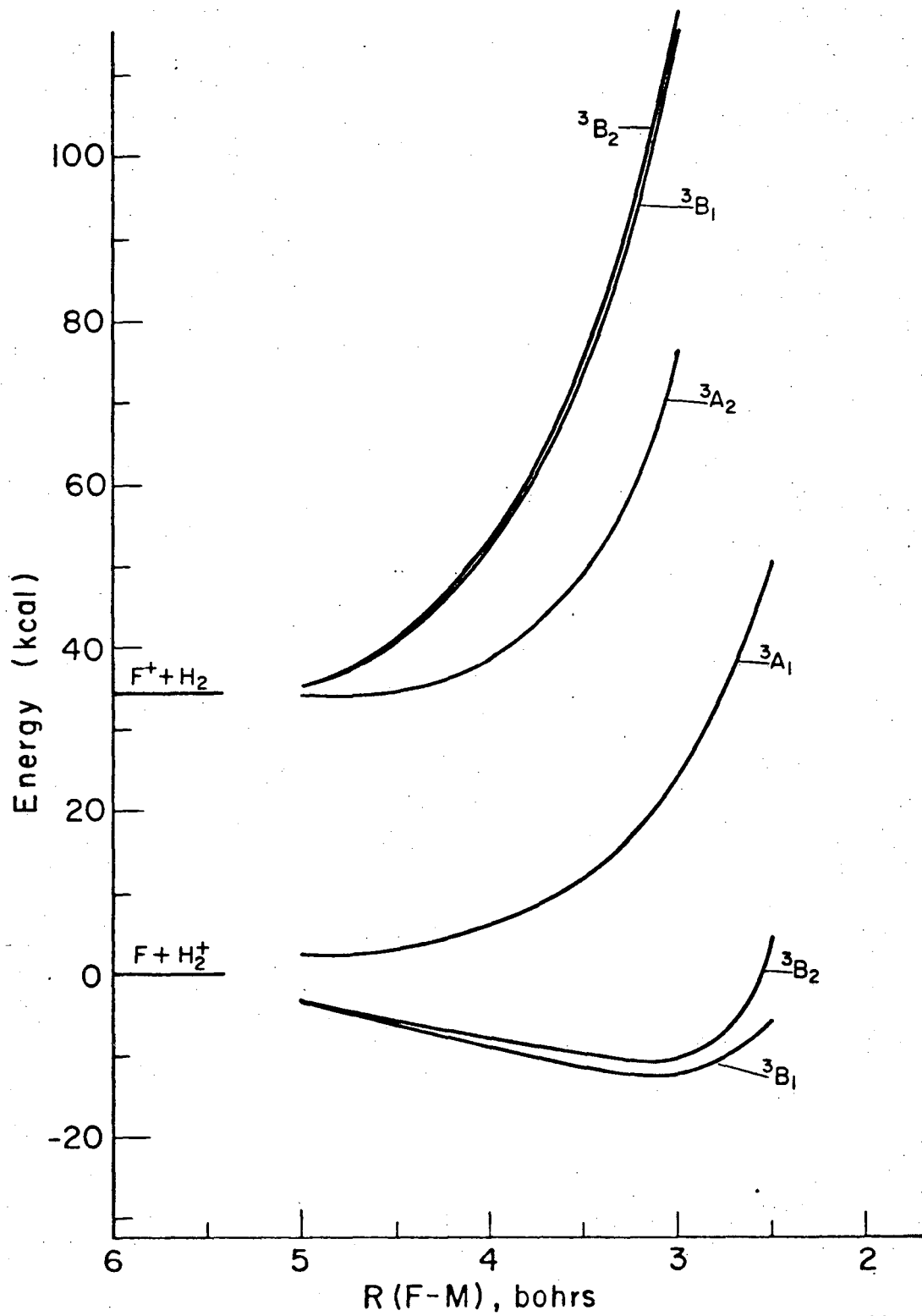
Figure 2. <u>Ab initio</u> correlation diagram for the $(F^+ + H_2, F + H_2^+)$ system. The C_{2v} results refer to the ground state FH_2^+ equilibrium geometry, i.e., they are vertical excitation energies. Similarly the $D_{\infty h}$ results were all obtained at $r_e(H-F) = 0.959$ Å, the optimum for the linear symmetric ground state. Note that the second $^3B_1$ state is very high, lying off the scale of the present figure.

Figure 3. Potential energy curves for the C_{2v} approach of F to H_2^+ with fixed bond distance $r(H-H) = 1.04$ Å; and of F^+ to $H_2 (r = 0.74$ Å$)$.

Fig. 1

$^3B_1$

$^3\Sigma_u^+$

$^3B_2$

$^3\Pi_g$

$^3B_2$

$^3A_2$

$^3A_1$

$^3B_1$

$^3\Pi_u$

$F^+(^3P) + H_2$

$F(^2P) + H_2^+$

$^1A_1$

$^1\Sigma_g^+$

Reactants

C_{2v}

$D_{\infty h}$

Energy (eV)

10

5

-5

-10

XBL778-3703

Fig. 2

-'\-

XBL778-3702

Fig. 3