quence at the site is considerably more secure than it was when the first ten radiocarbon dates were published in 1968 (*6*). We now have 26 radiocarbon dates and 4 recent thermoluminescence dates (*15*) from 1965–1966 and 1968 excavations, and the general outlines of the chronology seem apparent (Fig. 1). Particularly secure is the middle portion of the bronze period (Middle Period levels 3 through 6), which extends from 2300 to 900 B.C. For Early Period 3, however, the three dates are in conflict; a collagen date on skeletal material from the burial containing the copper tool (720 ± 95 B.C., sample I-5324) is in sharp disagreement with a thermoluminescence date on pottery from the same burial (2420 ± 200 B.C., sample PT-276), as well as with the 3600 B.C. date mentioned above (from a burial typologically very similar to the one in question). In view of the secure relative chronology afforded by the stratigraphy, the intersections of burials (203 from both excavations), and the distinctive styles of burial of each of the levels, I am unable to explain the collagen date. It can be combined with four other dates (two of them from a series of samples we suspect to have been contaminated) to form a "late sequence" (Fig. 1), but the "early sequence" of 12 dates appears much more reliable at present. In addition, these earlier dates are supported by several recent ones from other bronze-period sites in mainland Southeast Asia (*15, 16*). I know of no recent dates from the area which support the late sequence. I have discussed the problems involved in the chronology of the area in detail elsewhere (*2, 8*); at present, I believe that it is possible to say with a high degree of confidence that a well-developed bronze technology was present in mainland Southeast Asia prior to 2000 B.C. Moreover, this technology is very likely an indigenous one; no clear relationships link this technology with the Near East or the presumably later technologies of northern China and the Indus (*8*).

Given the evidence of numerous burial intersections, present between all pairs of adjacent levels except Early Period 3 and Middle Period 1, and the very rapid degree of change taking place in metal and ceramic technology during Middle Periods 1 and 2, I would conclude that the thermoluminescence date on Early Period 3 pottery is closer to the actual age of the burial than the indirect date of 3600 B.C. In view of the thermoluminescence dates of 2535 ± 200 B.C. (sample PT-278) and 2350 ± 150 B.C. (sample PT-279) on pottery from a Middle Period 1 burial, I would assume an estimate of about 2700 to 2500 B.C. for Early Period 3 and the first introduction of metal to the site. Hopefully the chronological problems will be solved in the near future, and this solution will allow investigators to pay closer attention to the more important questions of how and why the pervasive changes evident in the early Middle Period took place (*2*, p. 40).

D. T. BAYARD

Department of Anthropology,
University of Otago,
Dunedin, New Zealand

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Potential Energy Surface Including Electron Correlation for $F + H_2 \rightarrow FH + H$: Refined Linear Surface

Abstract. *A priori quantum mechanical calculations have been carried out at about 150 linear geometries for the fluorine plus hydrogen molecule system. An extended basis set of Gaussian functions was used, and electron correlation was treated explicitly by configuration interaction. Comparison with the experimental activation energy and exothermicity suggests that the theoretical potential surface is quite realistic.*

We have reported (*1*) an a priori quantum mechanical potential energy surface for the chemical reaction $F + H_2 \rightarrow FH + H$. About 350 individual calculations (each referring to a particular FH_2 geometry) were carried out, yielding a wealth of qualitative information about both the surface itself and the usefulness of various theoretical approaches to the calculation of potential surfaces. For example, the minimum energy path or reaction coordinate was found for a linear F-H-H arrangement, with the perpendicular approach of F to H_2 lying 12 kcal/mole higher. The calculations showed that a single configuration or Hartree-Fock wave function inevitably yields a barrier height or activation energy much greater than experiment. However, the explicit inclusion of electron correlation by way of configuration interaction (CI) results in a small barrier height, in qualitative agreement with experiment.

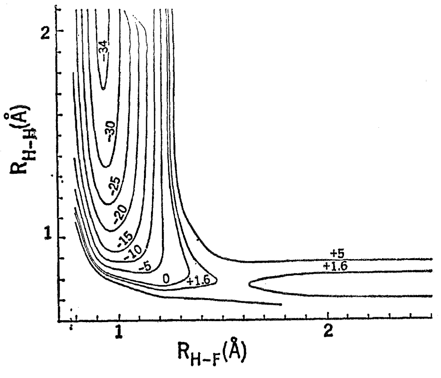

Fig. 1. Traditional contour map of the linear FH_2 potential energy surface.

Nevertheless, our preliminary $F + H_2$ surface (*1*) was not of "chemical accuracy," that is, of sufficient accuracy to be useful in detailed studies of the reaction dynamics. The principal problems with this first CI potential surface were (i) the predicted exothermicity was too small, 20.4 kcal/mole as opposed to the experimental value, 31.8 kcal/mole (*2*), and (ii) the predicted barrier height, 5.7 kcal/mole, was significantly higher than the experimental activation energy, 1.7 kcal/mole (*3*). We have now extended the basis set used previously and substantially reduced the above discrepancies with experiment.

Although the potential surface reported here is by no means expected to be perfect, we suggest that it corresponds fairly closely to reality. Since relatively little is known experimentally about the saddle point region of any A + BC potential surface, it is hoped that some of the features of this a priori surface will be useful for dynamical studies, that is, for classical trajectories (*4*), semiclassical treatments (*5*), and quantum calculations (*6*). Because there is a wealth of experimental information (*7*) concerning the dynamics of this reaction, an a priori F + H_2 surface seems particularly appropriate at the present time.

The primary difference between the present computations and our earlier work (*1*) concerns the basis set of contracted Gaussian functions (*8*). To our earlier F(4*s* 2*p*) and H(2*s*) basis we have added a set of 3*d* functions centered on fluorine and a set (p_x, p_y, and p_z) of 2*p* functions centered on each hydrogen. Since the importance of such "polarization functions" for predicting dissociation energies of diatomic molecules is well established (*9*), it follows that such functions should be used in studies of potential energy surfaces. Our preliminary calculations did not include polarization functions since they increase the computation times by about a factor of 3.

The initial stage in each calculation consisted of solving the restricted self-consistent-field (SCF) equations. This was followed by CI calculations of the "first-order" variety (*10*). The configurations selected were of the same types as those listed in (*1*), the only differences being due to the extension of the basis set. For each geometry an optimum set of molecular orbitals was obtained by using the iterative natural orbital procedure (*11*).

Calculations were carried out for about 150 linear F-H-H geometries. We hope that the qualitative features of the angular dependence of the FH_2 surface will be satisfactorily predicted by our earlier calculations (*1*). Note that the total energies of F + H_2 are −100.52568 (SCF) and −100.56202 (CI) Hartree atomic units, and for FH + H the calculations yielded −100.54701 (SCF) and −100.61691 (CI) Hartree atomic units (*12*).

Table 1. Summary of self-consistent-field (SCF) and configuration-interaction (CI) results for the F + H_2 reaction.

Property	SCF	CI	Experiment
Barrier height (kcal/mole)	29.3	1.66	1.7*
Exothermicity (kcal/mole)	13.2	34.4	31.8†
Saddle point geometry (Å)			
F-H	1.18	1.54	
H-H	0.836	0.767	

* Experimental activation energy (*3*). † See (*2*).

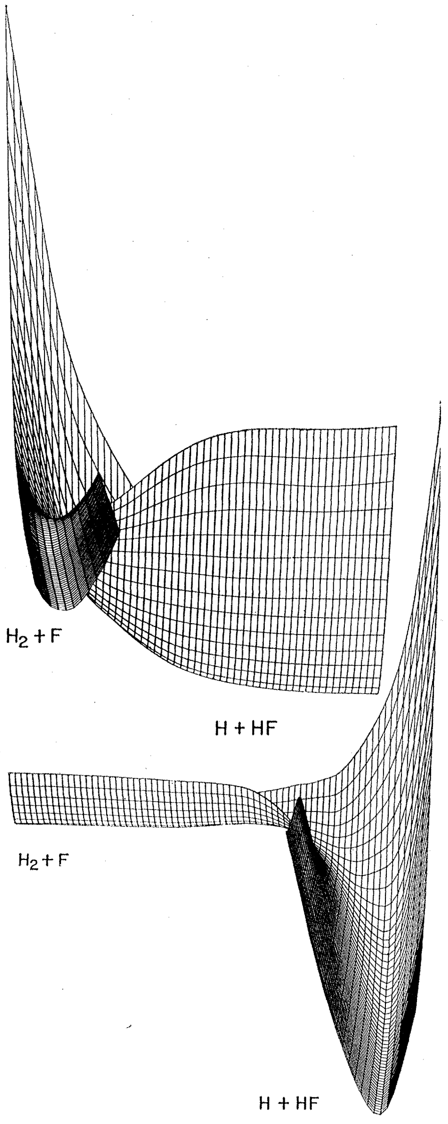

Fig. 2 (top). Electronic energy of linear FH_2 as function of F-H and H-H distances. Each small section bounded by four sides represents a square region in space, 0.05 Bohr on a side. Fig. 3 (bottom). Same as Fig. 2, but viewed from the exit channel FH + H.

Table 1 is a summary of the present results. The apparently perfect agreement with experiment for the CI barrier height is probably fortuitous. The experimental activation energy may be too low (*13*), and the barrier height is not (*14*) the same as the experimental activation energy, in any case. Muckerman (*15*) has suggested that for F + H_2 the barrier height is about 0.7 kcal/mole less than the activation energy. Nevertheless, the ab initio barrier height is quite close to the exact value. The SCF or single-configuration barrier height is much too large. The calculation in which electron correlation is taken into consideration predicts an exothermicity 2.6 kcal/mole (or 8 percent) larger than experiment. This small overestimation of the exothermicity appears to be an inherent feature of our theoretical approach and is not likely to be removed by further extension of the basis set. The saddle point geometry is not observable with available experimental methods, but our predictions agree well with the intuitive expectations of those familiar with the experimental aspects of the F + H_2 reaction (*16*).

A more detailed picture of the F + H_2 reaction is given by the minimum energy path, obtained (*1*) from the calculated total energies and shown in Table 2. Along this reaction coordinate, the H-H separation increases only slightly until the saddle point or transition state is reached. Farther along the reaction coordinate the H-H distance increases and the energy drops steadily, leading to separated FH + H. Three graphical representations of the FH_2 surface are shown in Figs. 1 to 3. Our calculated FH_2 surface is sufficiently accurate that these figures may be helpful to those with an interest in chemical kinetics, but no interest per se in the computation of potential surfaces.

Polanyi and co-workers (*17*) have developed methods for classifying exothermic A + BC potential surfaces as attractive, mixed, or repulsive. An attractive surface is expected to yield a high degree of vibrational excitation in the AB product molecule, while a repulsive surface should convert more of

Table 2. Minimum energy (E) path for $F + H_2 \rightarrow FH + H$. Distances ($R$) are in Bohr radii (*19*); 338-configuration first-order wave functions were used.

R_{H-F}	R_{H-H}	E (kcal/mole)	System
∞	1.42	0.00	Reactants
6.0	1.42	0.00	
4.0	1.42	0.25	
3.6	1.43	0.44	
3.4	1.43	0.75	
3.2	1.44	1.27	
3.0	1.44	1.61	
2.90	1.45	1.66	Saddle point
2.8	1.48	1.59	
2.63	1.5	1.18	
2.36	1.6	− 2.15	
2.03	1.8	−12.30	
1.85	2.0	−20.70	
1.80	2.2	−25.30	
1.78	2.5	−29.15	
1.77	3.0	−32.91	
1.76	∞	−34.44	Products

the exothermicity into product translational energy. Qualitatively, a surface is termed attractive if the exothermicity is released as the A atom approaches the BC molecule. In the same way, the surface is repulsive if the energy is released as AB and C separate. Mixed energy release is said to occur if the AB and BC internuclear separations simultaneously change as the energy is released. More quantitatively, several procedures have been proposed (*17*) for categorizing surfaces as percent attractive, mixed, and repulsive. Muckerman (*15*) applied these classifications to four semiempirical London-Eyring-Polanyi-Sato (LEPS) (*18*) surfaces for FH_2. By Polanyi's rectilinear method, three of the four surfaces were found to be 0 percent attractive and 100 percent repulsive. Our ab initio surface is also 100 percent repulsive by the rectilinear method. We have also categorized the present surface by Polanyi's minimum path method and find 23 percent attractive, 22 percent mixed, and 55 percent repulsive. This minimum path characterization is far more flexible than the rectilinear, which (taken literally) might lead one to expect all the exothermicity to be converted to product translation. Further, the simple minimum path description of our surface is consistent with the experimental finding (*7*) that the $F + H_2 \rightarrow FH + H$ reaction yields a large amount of FH vibrational excitation (approximately 67 percent of the exothermicity).

A feature not apparent from the minimum energy path or the graphics is a small long-range attraction between FH and H. When diatomic FH is held at its experimentally determined equilibrium internuclear separation, 1.7328 Bohrs (*19*), this attraction is strongest at an H-H distance of 4.75 Bohr radii and amounts to 0.24 kcal/mole (or 120°K) in our CI calculations. This attraction is predicted to be 0.25 kcal/mole from the present SCF calculations, and it was 0.22 kcal/mole in our earlier work (*1*). Jaffe and Anderson (*20*) have carried out classical trajectory calculations for $F + H_2$ on a modified LEPS potential surface with an attraction of 4.8 kcal/mole between FH and H. Our calculations suggest that such a large attraction is not realistic. Finally, the present computations do not predict a long-range attraction between F and H_2.

For systems with more than three electrons, a priori potential energy surfaces approaching quantitative accuracy are now feasible. Our methods can be extended to the study of potential surfaces for several distinctly different types of $A + BC$ reactions, including $H + F_2$ (calculations now in progress), $Li + HF$, and $Li + F_2$.

CHARLES F. BENDER
Lawrence Livermore Laboratory,
University of California,
Livermore 94550
STEPHEN V. O'NEIL, PETER K. PEARSON
HENRY F. SCHAEFER III
Department of Chemistry and
Lawrence Berkeley Laboratory,
University of California,
Berkeley 94720

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Chlorination at Power Plants: Impact on Phytoplankton Productivity

Abstract. *Studies of the effects of passage through a power plant on river phytoplankton have shown that chlorination depresses rates of photosynthesis and respiration to a much greater extent than does heating.*

The addition of chlorine in the form of hypochlorite or as gaseous chlorine is a procedure carried out several times daily in the routine operation of power-producing plants and sewage-processing plants. As a bacteriocide, chlorine acts as an antifouling agent in the costly hardware of cooling systems and as reducer of biological oxygen demand at the site of sewage release (thus moving the problem downstream). As the number of installations pouring chlorine into our waterways increases, the total chlorine load increases, and chlorine effects are exacerbated.

We can find nowhere in the literature a presentation of the direct relationship between chlorine concentration and productivity of phytoplankton, nearly all emphasis having been placed on heating and sudden thermal shock (*1*). The relationship has been referred to, however (*2*). Although anxious to avoid minimizing the many effects of heating river water we contend that the very specific effect of depression of plankton photosynthesis (PS) and respiration (R) in the vicinity of power plants in routine operation is for the most part due to the addition of chlorine.

We determined rates of PS and R by using the light-dark bottle incubation technique and determined changes in