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Theoretical Studies of the Potential Surface for the F + $H_2 \rightarrow$ HF + H Reaction

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Abstract

The F + $H_2 \rightarrow$ HF + H potential energy hypersurface has been studied in the saddle point and entrance channel regions. Using a large [5*s* 5*p* 3*d* 2*f* 1*g*/4*s* 3*p* 2*d*] atomic natural orbital basis set, we obtain a classical barrier height of 1.86 kcal/mole at the CASSCF/multireference CI level (MRCI) after correcting for basis set superposition error and including a Davidson correction (+Q) for higher excitations. Based upon an analysis of the computed results, the true classical barrier is estimated to be about 1.4 kcal/mole. We also compute the location of the bottleneck on the lowest vibrationally adiabatic potential curve, and determine the translational energy threshold from a one-dimensional tunneling calculation. Using the difference between the calculated and experimental threshold to adjust the classical barrier height on the computed surface yields a classical barrier in the range of 1.0-1.5 kcal/mole. Combining the results of our direct estimates of the classical barrier height with the empirical values obtained from our approximate calculations of the dynamical threshold, we predict that the true classical barrier height is 1.4± 0.4 kcal/mole. Arguments are presented in favor of including the relatively large (≈1 kcal/mole) +Q correction obtained when nine electrons are correlated at the CASSCF/MRCI level.

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I. Introduction

The F + H_2 → HF + H reaction is a prototype in the field of gas phase reaction dynamics, since it is accessible to both detailed theoretical and experimental study. Early electronic structure studies of this reaction by Bender *et al.* [1], using first-order CI wave functions in a DZP basis set, gave a barrier height of 1.7 kcal/mole, but recent more extensive *ab initio* calculations by Frisch *et al.* [2] gave a barrier height greater than 3.2 kcal/mole. In a recent review article, Schaefer [3] reiterated his position that the energy barrier for this reaction on the lowest Born-Oppenheimer potential energy surface (PES) must be greater than the 2.35 kcal/mole value deduced in an earlier study by Ungemach *et al.* [4]. Further, using a harmonic vibrational analysis, it was argued that this "classical" barrier height is consistent with the observed experimental translational energy threshold [5] for the reaction (about 0.8 kcal/mole) when zero-point corrections are included. On the other hand, Steckler *et al.* [6] carried out canonical variational transition state theory (VTST) calculations, including the effects of vibrational anharmonicity and multidimensional tunneling corrections, using a global empirical potential energy surface with a 2.7 kcal/mole barrier and other saddle point properties based on the Frisch *et al.* [2] surface. They concluded that the barrier from that work must be significantly too high, since the VTST calculations produced a thermal rate constant at 190K that was about 30 times smaller than experiment. They also argued that the zero-point vibrational energy correction is much smaller, because the VTST bottleneck for the reaction is shifted much further out in the entrance channel from the classical barrier, and showed that it is important to include anharmonic effects in the threshold determination. Recently, Truhlar and coworkers [7-9] have reexamined the saddle point region on the F+H_2 PES using a multireference CI (MRCI) description. They attempt to reach both the one-particle and n-particle limits using the scaled external correlation (SEC) method [10]. For collinear geometries, their SEC energy barrier is 1.6 kcal/mole, much lower than previous MRCI calculations as well as recent studies using the quantum Monte Carlo method [11]. Also, they find that the MRCI+Q (where +Q denotes the multireference Davidson correction for higher excitations) and the SEC bending potentials exhibited additional minima for nonlinear geometries. Their extremely flat bending potential is significantly different from those implicit in empirical LEPS surfaces such as the commonly used Muckerman surface No. 5 [12], and the first-order CI calculations of Bender *et al.* [13].

In this work we consider several aspects of the F + H_2 PES. First, we present a study of the classical barrier height as a function of improvements to both the one-particle and n-particle treatments. Recent advances [14] in strategies for basis set contraction, which allow the use of very large primitive basis sets, enable us to approach the one-particle basis set limit. We also are able to use a higher level of correlation for calibration than in previous treatments. Second, using the externally contracted CI method (CCI) [15], bending potentials were computed in the collinear saddle point region. Our best computed bending potential favors a non-collinear approach, but by a lesser extent than does the SEC bending potential of Schwenke *et al.* [8]. Third, the calculated CCI surface was used to locate the bottleneck on the vibrationally adiabatic potential curve, and the reaction threshold was deduced from a one-dimensional tunneling calculation. We estimate the true classical barrier height by adjusting the CCI barrier height for the difference in the calculated and experimental thresholds. In the next section we discuss the details of the calculations such as basis sets, choice of active spaces in the orbital determinations and correlation treatments. In Section III we discuss our study of the one-particle and n-particle requirements for a direct *ab initio* computation of the classical barrier height. In Section IV we discuss our attempts to characterize an accurate vibrationally adiabatic potential curve for both F + H_2 and F + D_2. Our conclusions are presented in Section V.

II. Computational Details.

The primitive basis for fluorine is the (13*s* 8*p*) set of van Duijneveldt [16], augmented with a (6*d* 4*f* 2*g*) polarization set. The polarization functions are taken as even-tempered sequences with an internal ratio of 2.5. The geometric mean of the *d* exponents is 1.62, while the *f* and *g* sets are based on multiplying this mean *d* exponent by 1.2 and 1.44, respectively. This primitive set is contracted to [5*s* 4*p* 3*d* 2*f* 1*g*] using a general contraction scheme based on atomic natural orbitals (ANOs) [14]. This basis is further augmented by an additional even-tempered diffuse 2*p* function to better describe F^- character (α=0.059326). The primitive basis for hydrogen is the (8*s*) set of van Duijneveldt [16], augmented with a (6*p* 4*d*) polarization set. The *p* and *d* sets are even-tempered sequences with an internal ratio of 2.5 and geometric means of 1.0. The hydrogen *f* basis set consists of three even-tempered primitive f functions with a geometric mean exponent of 1.0. This primitive set is contracted to $[4s\ 3p\ 2d\ 1f]$ using ANOs from a calculation on H_2, as described by Almlöf and Taylor [14]. The sets described here are the largest contracted sets used in the present work: smaller sets were obtained by deleting ANOs as required. The $3s$, $4p$, $5s$ and $5d$ combinations of the $3d$, $4f$ and $5g$ functions, respectively, are deleted in all calculations.

For all collinear geometries, the SCF configuration of the $F+H_2$ $^2\Sigma^+$ surface connecting reactants and products is:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi^4,$$

where 1σ and 2σ are nominally the fluorine $1s$ and $2s$ orbitals. In the reactants channel, the 3σ orbital is the H_2 bonding orbital ($1\sigma_g$), and the 4σ and 1π orbitals are predominantly the fluorine $2p$ orbitals. This reference configuration was used for all of our single-reference based correlation treatments, which included singles plus doubles CI (SDCI) and the coupled pair functional (CPF) method [17].

CASSCF wave functions were used as the starting point for our multireference CI (MRCI) treatments. The minimum active space that gives a reasonable first-order description of this system comprises the 3σ-5σ orbitals. For the reactants channel, the 5σ orbital corresponds to the H_2 $1\sigma_u$ orbital. In C_{2v} symmetry this is denoted as a (300) active space, where the integers denote the number of active a_1, b_1 and b_2 orbitals. When the 1π orbital is included in the active space to give a (311) CASSCF, the number of configurations is increased only slightly. The barrier is not significantly changed when the MRCI calculation is based on the larger (311) space. It is well known that $2p \rightarrow 2p'$ correlation is important in accurately computing the electron affinity (EA) of F and O [18], as well as in describing HF and OH owing to the large fraction of F^- and O^- character in the wave function. In the course of the reaction $X+H_2 \rightarrow HX + H$, the degree of X^- character in the wave function increases. It is, therefore, not surprising that Liu [19] has found that inclusion of $2p \rightarrow 2p'$ excitations in the CASSCF and MRCI reference space significantly (0.8 kcal/mole) reduced the barrier height for the $F+H_2$ reaction. This has also been found for $O(^3P)+H_2$ by Walch [20]. Thus to accurately compute the $F+H_2$ barrier, the 2p′ shell must be included in the CASSCF resulting in a (422) active space. However, the fourth a_1 orbital is only weakly occupied and essentially of the same importance as the $2\sigma_g$ orbital in H_2. Thus either a (322) or (522) CASSCF active space must be used to eliminate the possibility of multiple solutions. The (522) active space is sufficiently flexible to correlate both the F $2p$ orbital and to provide radial correlation for H_2. Alternatively, as discussed below, a (322) active space, which takes into account most of the effect of 2p→2p′ excitations, can be used at less expense than the (522) active space.

The calculation of a smooth bending potential about the collinear saddle point required an additional expansion of the active space. Two problems occurred when the (322) active space (denoted (52) in C_s symmetry) was used for non-collinear geometries. First, this active space includes the 2p′ orbitals, which correlate the doubly occupied fluorine 2p orbitals, but not the singly occupied one. For collinear geometries this is a reasonable choice based on natural orbital occupations, but for large bending angles this wave function changes discontinuously. For angles $\theta > 75°$, (θ=180° − ∠(HHF)), the 2pσ correlation is more important than the H_2 left-right correlation, which leads to a change in character of the most weakly occupied CASSCF orbital. Thus, the calculation using the collinear-derived active space is not adequate for larger θ values needed to establish the shape of the potential curve. Second, there is a competition between $2s$ and $2p$ correlation, which leads to a mixing of the fluorine $2s$ and the in-plane doubly occupied $2p$ orbital. This causes symmetry breaking of the orbitals for collinear geometries when treated in C_s symmetry, resulting in a discontinuity between bent and linear structures. Adding the other component of $2p'$ leads to a (62) active space, while also adding the fluorine $2s$ and $2s'$ orbitals leads to an (82) active space. As shown in Fig. 1, smooth bending potentials are obtained only when the correlation treatment is based on the (82) active space— see Section IV.

Multireference treatments using both the MRCI method and the externally contracted CI (CCI) method of Siegbahn [15] have been performed from several active spaces. For the (322) and larger reference spaces, the complete second-order treatment is prohibitively large, thus necessitating reference selection. Therefore, we include an occupation in the reference space only if the absolute value of the coefficient of one of its component spin couplings in the CASSCF wave function is above a designated threshold. Thresholds of 0.05, 0.025 and 0.01 are used in this work. In each case the multireference analog of Davidson's correction [21] was added to account for the contribution from unlinked quadruple excitations. The correction in the MRCI case is $\Delta E\ (1 - \sum_R C_R^2)$ where the C_R are the coefficients of the reference configurations in the MRCI wave function and ΔE is the energy difference between the reference and MRCI wave functions. In the CCI case this expression is divided by $\sum_R C_R^2$. The results where Davidson's correction has been applied are denoted by MRCI + Q or CCI + Q.

Since the CCI method is less expensive than the MRCI method, it allowed us to use larger configuration state function (CSF) expansions, to consider a larger number of geometries on the F + H_2 surface, and to investigate the effects of further basis set extensions. At the CCI(CCI+Q) level using a 0.025 selection threshold and the [5*s* 5*p* 3*d* 2*f* 1*g*/4*s* 3*p* 2*d*] ANO basis set, the collinear barrier height is 2.79(2.02) kcal/mole, which is about 0.2–0.4 kcal/mole larger than at the MRCI level. Removing the *g* function leads to a barrier height of 2.89(2.15) kcal/mole. This 0.1 kcal/mole basis set expansion error was deemed small enough that the [5*s* 5*p* 3*d* 2*f*/4*s* 3*p* 2*d*] basis set was used to generate a 20-point grid in r_{HF} and r_{HH}, which spanned the saddle point and dynamical bottleneck for the entrance channel region of the PES. To verify that the restrictions inherent in the CCI approach do not significantly alter the shape of the surface, MRCI calculations were carried out for nine collinear geometries centered around the saddle point and at the bottleneck geometry. The MRCI+Q and CCI+Q quadratic force constants at the saddle point differ by less than 10%. The difference in energy between the saddle point and bottleneck geometry is 0.19 kcal/mol (MRCI+Q) versus 0.28 kcal/mole (CCI+Q). The effect of these uncertainties in the CCI+Q potential on the computed threshold is discussed in Section IV.

The CCI potential calculations were carried out on the CRAY X-MP/48 with the MOLECULE [22]-SWEDEN [23] system of programs. The very large MRCI calibration calculations were done primarily on the NAS CRAY 2. The CPF calculations were done on the Cyber 205 using the Karlsruhe codes [24].

III. Studies of the classical barrier height

In Table I we compare, at the 7-electron level (H1*s* and F2*p*) of correlation, various MRCI (and MRCI+Q) treatments with the full configuration-interaction(FCI) treatment using the [4*s* 3*p* 1*d*/2*s* 1*p*] ANO basis set: this is an expansion of the approximate treatments of the correlation problem reported in Ref. 25. The entries are denoted both by the active space and by the reference threshold selection criterion. Most noteworthy is that the barrier heights are in much better agreement with the FCI after a correction is made for quadruple excitations. Also, the magnitude of the +Q correction decreases as the reference threshold is lowered. Further, the barrier height varies much less with selection threshold if a +Q correction is included. For the larger (522) active space the +Q correction does slightly overshoot the FCI result. Similar conclusions can be drawn from part B of Table I, where we have optimized the geometry at each level of treatment using a biquadratic fit to a grid of nine points. Both the geometry and barrier height are generally in better agreement with the FCI after the +Q correction is added. Although the +Q correction may be too large in the limit of a SOCI calculation (i.e. no reference selection), we have observed that the MRCI+Q results are often superior to the MRCI if the reference configurations are selected. We also believe that the +Q correction is even less likely to be too large when 9 electrons are correlated, but unfortunately we are unable to carry out the necessary FCI calibration calculations for a realistic one-particle basis. However, the observations made in our study of the electron affinity [26] of oxygen are probably also valid here. It appears that $2s$ correlation increases the electron affinity of oxygen (by as much as 2.5 kcal/mole), but that a very high level of correlation treatment is required to fully account for this effect. Our work suggests that to obtain a quantitative barrier height for $F+H_2$ it is not only necessary to explicitly include $2p \rightarrow 2p'$ correlation, but also to fully account for differential effects from $2s$ correlation.

Based upon our calibration calculations, the threshold for reference selection in the ANO basis set calculations is chosen as 0.0 (no selection) for the MRCI(300) reference space and 0.025 in all other cases. For example, in the MRCI(322) treatment, the final reference list is obtained by merging the important occupations for $F+H_2$, HF+H and the MRCI(300)+Q saddle point barrier geometry. This leads to 12 reference occupations (29 CSFs), and an MRCI expansion of 1 343 112 CSFs when 9 electrons are correlated.

In Table II we have summarized our results for the reactants H_2 and HF as well as our calculated basis set superposition errors (SE). Our results for both diatomics are in very good agreement with experiment [27]. For HF, the errors are only 0.002-0.003 a_0 for r_e and 0.05-0.06 eV for D_e, for calculations using the (222) active space. The basis set SE have been computed using the counterpoise method [28] including the full space of the ghost basis. The basis set superposition errors for H_2 in the presence of the F basis are only about 0.01 kcal/mole. The basis set superposition errors for F in the presence of the H_2 basis are also quite small, especially if the 2s electrons are not correlated. The superposition errors for F^- in the presence of the H_2 basis are much larger than those for F. However, Mulliken population analysis shows that in the saddle point region, the wave function possesses only about 5% F^- character. Hence it is appropriate to use the SE for F in Table II to correct our barrier heights; approximately 0.1 and 0.2 kcal/mole should be added to the 7-electron and 9-electron barrier heights, respectively. The values in the tables were not corrected, since the remaining basis set incompleteness effects are probably of the same magnitude and of opposite sign.

In Table III we summarize our theoretical studies of the classical saddle-point geometry and barrier for the F + H_2 reaction. Our MRCI(300) treatment in the [5*s* 5*p* 3*d* 2*f* 1*g*/4*s* 3*p* 2*d*] ANO basis yields a barrier height and saddle-point geometry in good agreement with the large Slater basis set calculations of Frisch *et al.* [2]. This is especially true after the Slater calculations are corrected for their larger basis set superposition error (see Table II). Adding a +Q correction to the MRCI(300) result reduces the barrier by about 1.2 kcal/mole and shifts the saddle point by over 0.1 a_0 further out in the entrance channel. Another substantial reduction of the barrier height occurs when the MRCI is based upon the (322) active space, which includes $2p \rightarrow 2p'$ excitations; the effect is very similar in magnitude to that found by Liu [19]. The +Q for this active space has a smaller, but still very large, effect on the barrier height. If 2*s* correlation is not included, the barrier height is slightly higher and the magnitude of the differential +Q correction is smaller by a factor of about one half. The exothermicity of the reaction is also increased substantially, but interestingly the saddle-point geometry does not change significantly. Of the two single-reference based entries in Table III, the CPF method is in better agreement with the MRCI(322)+Q than SDCI+Q for both the saddle point geometry and barrier, although it is inferior to the MRCI-based methods for the exothermicity. It should also be noted that the addition of the +Q correction at the MRCI(322) level reduces the size consistency error, making the supermolecule exothermicity nearly equal to the value computed using the fragment dissociation energies.

In the remainder of Table III we present some calibration calculations using the CCI method. We find that adding an *f* ANO to the hydrogen basis decreases the barrier by 0.06(0.07) kcal/mole at the CCI(CCI+Q) level. Furthermore, removing the *g* function from fluorine increases the barrier by 0.11(0.13) kcal/mole. Apparently, then, basis set improvements decrease the barrier height. Considering that the SCF and CASSCF barriers are quite large, the barrier height tends to decrease monotonically when improvements are made in the level of correlation treatment that recover successively larger percentages of the differential correlation energy between the reactants and the saddle point. In the following discussion we attempt to assign upper bounds of varying rigor to our *ab initio* calculations. A very conservative upper limit of 2.52 kcal/mole is given by the 7-electron MRCI(322)−SE+Q calculation, since this MRCI is calibrated against FCI calculations, and we know that 2*s* correlation reduces the barrier. Since the 7-electron +Q correction is not likely to be an overestimate, based on the FCI calibration calculations, the value of 2.26 kcal/mole obtained by the 9-electron MRCI(322)−SE +Q(7-electron) is also a conservative upper bound. Since the +Q correction is less likely to overshoot as more electrons are correlated, we expect that our 9-electron MRCI(322)−SE+Q result of 1.86 kcal/mole is a realistic estimate. However, our best estimate for the barrier includes a correction for remaining basis set incompleteness, as discussed above, and a larger +Q correction, which we feel is justified from studies of the electron affinities of oxygen and fluorine. Thus instead of correcting for basis set superposition error we assume that the basis set limit is actually 0.1 kcal/mole less than the directly computed value. A justifiable lower bound of 1.35 kcal/mole for the barrier height is obtained by using 120% of the +Q correction. Although this latter value is below the directly computed values, the extrapolations seem well justified based on analogous studies of the electron affinity of oxygen, which indicate that the full effect of higher excitations and 2*s* correlation are difficult to incorporate into the MRCI calculations. These lower values are consistent with extrapolations of Truhlar and coworkers [7-9] using the SEC method. Further, they are consistent with estimates obtained using VTST and our *ab initio* bending potentials as discussed in the next section. Based only upon our *ab initio* calculations, the classical barrier height is, therefore, estimated to be between 1.35 and 1.86 kcal/mole.

IV. Studies of the vibrationally adiabatic potential curve

It is well known that, for gas phase reactions, the "classical" barrier height on the PES is only approximately related to the experimental activation energy or threshold energy. Indeed, for F+H_2 previous studies [2,3,7-9] have shown that zero-point vibrational energy effects may be as large as 50% of the computed barrier height. Therefore, to better characterize the saddle point and entrance channel regions of the potential energy surface, a grid of 20 collinear geometries was obtained at the CCI(322) level. These points encompassed the dynamical bottleneck region. A bending potential was then computed with r_{HF} and r_{HH} held fixed at approximately their collinear saddle point values (r_{HF} =2.90 a_0 and r_{HH} =1.45 a_0). An explicit tabulation of this CCI potential energy grid is available from one of the authors (SPW). The bending potentials computed with the (52), (62) and (82) active spaces (denoted in C_s symmetry) are illustrated in Fig. 1. Each of these CCI+Q bending potentials was generated using a reference space that included all CSFs with coefficients greater than 0.025 in the CASSCF wave functions (merged list for representative bending angles). As the F+H_2 geometry is not included in the selection of references, these calculations are not appropriate for computing the actual barrier height, and hence are used only to compute the bending potential. Only the (82) curve shows a smooth variation with angle. The effects of symmetry breaking are illustrated by the (62) bending curve. The connected points for the (62) bending curve were all performed using C_s symmetry and this potential is similar to the (82) potential, but not as smooth. The single point in Fig. 1 is for a collinear calculation in C_{2v} symmetry. If θ = 0° were to pass through this point, instead of the broken symmetry point, then a curve very similar to the (52) curve would be obtained. Interestingly, the orbitals from the (52) CASSCF calculation do not break symmetry for collinear geometries computed in C_s symmetry. However, the non-collinear geometries do exhibit mixing of the fluorine 2*s* and in-plane doubly occupied 2*p* orbitals, and the maximum at 15° in the (52) potential is believed to be nonphysical. It is interesting to note that the upper curves in Fig. 1 resemble the MRCI+Q and SEC bending potentials of Schwenke *et al.* [8] in that they exhibit minima at θ=0° as well as at larger angles.

The (82) bending potential, shown in Fig. 1, is very flat up to $\theta \approx 60°$, but rises fairly sharply for larger θ values. For this choice of active space, the CCI and CCI + Q bending potentials are very similar. The angle variation is only carried to θ = 105°, because for that angle the structure has approximately C_{2v} symmetry with the F nearly equidistant from the two H atoms. It is interesting to note that the energy at that geometry is only 2.37 kcal/mole higher than at the collinear saddle point in the CCI calculations (1.81 kcal/mole higher in CCI+Q). This means that the potential energy surface is rather isotropic with respect to the F atom approach to the H_2 molecule. The actual minimum in the CCI bending potential occurs for $\theta \approx 60°$, but the bent structure is only 0.04 kcal/mole below the collinear saddle point structure (0.12 kcal/mole lower at the CCI+Q level). This bending potential is qualitatively similar to the one obtained by the SEC method [8], except that the SEC method predicts a stronger energetic preference for non-collinear geometries (by about 0.3 kcal/mole) than does the present calculation and has an additional energy minimum at 180°. In fact, the SEC bending potential more closely resembles the (52) CCI+Q bending potential drawn in Fig. 1. The Bender *et al.* [13] bending potential also predicts the minimum energy approach to be slightly noncollinear, but their potential rises somewhat more steeply for larger θ values.

Canonical variational transition state theory (VTST) [29] has been shown to provide a good estimate of rate constants for simple gas phase reactions. In this approach, the transition state is located at the free energy "bottleneck" between reactants and products, and the rate constant is computed from transition state theory with corrections for tunneling and recrossing effects. To locate the variational transition state, the triatomic vibrational frequencies along the minimum energy path for F + H_2 collisions must first be determined.

The bending contribution was determined from the one-dimensional bending potential by numerical integration of the vibrational Schrödinger equation with fixed r_{HH} and r_{HF}. This computation used a standard diatomic vibrational energy code with the bending angle θ scaled by $\sqrt{r_{HF} r_{HH}}$. The bending potential energy curve was represented by a bicubic spline fit. The effective reduced mass was taken to be

$$\mu_{eff} = \frac{m_H m_F r_{HH} r_{HF}}{m_H r_{HH}^2 + m_F r_{HF}^2 + m_F (r_{HH} + r_{HF})^2},$$

which comes from the scaled Wilson G-matrix element [30] for the bending coordinate of a linear triatomic molecule. To validate this approach, we performed a test calculation for a quadratic-quartic potential with known energy levels. Our approach obtained excellent agreement for the three lowest energy levels, and only small inaccuracies for the higher levels. The resulting energy levels for the F-H-H and F-D-D systems with the CCI+Q bending potential shown in Fig. 2 demonstrate that the energy levels are rather anharmonic, and that the zeroth level lies slightly above the energy maximum found in the bending potential at collinear geometry.

Therefore the reference reaction path for this reaction can be taken to be collinear even though the bending potential shows a slight preference for bent geometries. As the contribution to the zero-point energy from the bending mode in F + H_2 and F + D_2 at the collinear saddle point is fairly small, and goes to zero for the separated reactants, it is a reasonable assumption to consider it to be constant along the minimum energy path (MEP) in the vicinity of the dynamical bottleneck.

The next step in locating the variational transition state is to determine the symmetric and asymmetric stretching frequencies along the MEP. To do this we fitted the 4×5 grids of collinear CCI and CCI+Q energies to bicubic polynomials in r_{HF} and r_{HH}. Note that there is a substantial difference in both the saddle point geometry and in the zero-point correction when a more accurate bicubic polynomial is used instead of a simple biquadratic form to represent the surface. For example, at the CCI level, when the bicubic polynomial is used instead of a biquadratic one, the saddle point shifts to shorter r_{HF} by about 0.03 a_0 and the zero-point correction increases by 0.09 kcal/mole. These differences are slightly larger for the CCI+Q case. These relatively large changes are a consequence of the extremely flat potential surface. Using the bicubic polynomial fits, we then determined the MEP as a function of r_{HF} by interpolation, and computed the normal mode vibrational frequencies at points along the MEP by standard methods [30]. The adiabatic ground-state potential curves for F+H_2 and F+D_2 are shown in Fig. 3. These curves were determined by adding the differential vibrational zero-point energy correction to the CCI(CCI+Q) energy along the MEP. The zero-point correction was taken as half the $H_2F(D_2F)$ symmetric stretch mode frequency plus twice the $H_2F(D_2F)$ zeroth-bending level, less half ω_e for $H_2(D_2)$. The magnitude of the anharmonic correction to the symmetric stretch normal mode was estimated by fitting a Morse potential to the second and third derivatives of the potential energy profile along the direction of the symmetric stretch normal mode. In all cases, the value of $\omega_e x_e$ obtained was within 20 cm^{-1} of the value for H_2 or D_2, and thus including anharmonic effects for reactants and transition state would alter the zero-point energy correction by 0.02 kcal/mole or less. Since the shift in r_{HF} between the classical and adiabatic barrier is approximately an order of magnitude greater than the corresponding shift in r_{HH}, we have used internal coordinates in the present study. The differences between using internal coordinates and mass scaled cartesian coordinates for determining the reaction coordinate and symmetric stretch directions (and their appropriate reduced masses) are expected to be insignificant owing to the small reaction path curvature.

In Table IV we summarize the computed zero-point and tunneling contributions to the computed threshold for the F + H_2 and F + D_2 reactions. The results labeled "E barrier" are for the analysis of the classical barrier location, and manifest a substantial zero-point effect. For CCI + Q, the saddle point symmetric stretch frequency (predominantly H_2 stretch) is 3768 cm^{-1} compared to 4401 cm^{-1} for free H_2, while the lowest eigenvalue for the bend potential is 45.9 cm^{-1} leading to a zero-point correction of 0.64 kcal/mole. A one-dimensional tunneling correction was determined by fitting the classical potential $V_{MEP}(s)$ to an Eckart barrier [31] (we matched the curvature at the barrier of the MEP, and adjusted the exothermicity to minimize the root-mean-square deviation between the Eckart potential and $V_{MEP}(s)$). We assumed the experimental threshold energy corresponds to a reaction cross section equal to 25% of its value when the translational energy equals the barrier height. This tunneling correction further reduces the barrier by about 0.5 kcal/mole leading to a translation energy threshold of 1.0 kcal/mole for a 2.1 kcal/mole high barrier. As the experimental threshold is $\approx$ 0.7 kcal/mole, this would suggest that the true barrier height is about 1.8 kcal/mole. However, when the same analysis is carried out on the adiabatic ground-state potential curve (labeled "adiabatic barrier"), the dynamical bottleneck is found to occur at r_{HF} = 3.16 and r_{HH} =1.42, a shift in r_{HF} of 0.25 a_0 from the computed saddle point geometry. At this geometry, the H_2 stretching frequency is 4178 cm^{-1} and the zero-point correction, while still lowering the barrier, is only 0.06 kcal/mole. The resulting adiabatic barrier height is 1.86 kcal/mole. Inclusion of an equivalent one-dimensional tunneling correction leads to an estimated translational energy threshold of 1.5 kcal/mole, which is about 0.6 kcal/mole lower than the classical barrier height. This implies that the classical barrier on the exact *ab initio* potential energy surface should be approximately 1.3 kcal/mole. This barrier height is significantly below the 2.35 kcal/mole estimate of Schaefer [3,4], and also slightly below our best estimate based upon direct calculation.

We applied the same analysis to both the F + H_2 and F + D_2 reactions using the CCI and CCI+Q results in both cases. Interestingly, for F + D_2 the tunneling factor is in general smaller, but the shift in energy between the adiabatic barrier and saddle point is larger. The resulting translational energy threshold predictions, which are nearly the same for both reactions, are estimated to be 0.67± 0.05 kcal/mole below the saddle point energy on the potential energy surface. On the other hand, if the zero-point and tunneling corrections are applied at the classical barrier geometry, the F+D_2 reaction has a 0.24 kcal/mole larger threshold energy.

It is difficult to assess the uncertainty in this method of predicting the barrier height. Neumark *et al.* [5] easily observed reactive scattering in the F + H_2/D_2 crossed molecular beam experiments at reactive collision energies of 0.7-0.8 kcal/mole, but did not give an estimate of the magnitude of the cross section. We have chosen to assign the tunneling correction to the threshold as the translational energy for which the tunneling probability is 0.125 (25% of the value at the barrier energy). While Steckler *et al.* [6] concluded that the Eckart tunneling correction worked well for this system, there probably still is an uncertainty of ±0.2 kcal/mole in this value (due in part to determining the magnitude of the cross section at the experimental threshold). The tunneling correction is significantly smaller for the adiabatic barrier than for the classical barrier, owing to a broader barrier with reduced curvature (as manifested by a smaller imaginary asymmetric stretch frequency). This effect is more pronounced for the CCI+Q results, which have significantly lower barriers than do the CCI. In addition, the change in curvature at the adiabatic barrier between F+H_2 and F+D_2 nearly counteracts the mass effect and results in approximately equal tunneling corrections for the two reactions.

The other uncertainties in the analysis are easier to assess. The vibrational zero-point correction is sensitive to the saddle-point location, which should be accurately determined at this level of theory. One measure of the remaining error is the approximately 10% difference between the MRCI+Q and the CCI+Q force constants. For the vibrational frequencies along the minimum energy path we have used the energy levels of the actual CCI bending potential and demonstrated the unimportance of correcting for anharmonicity in the stretching coordinate. The energy difference between the adiabatic barrier and the saddle point is estimated to contain an uncertainty of ±0.1 kcal/mole. Combining these two error estimates, we believe the energy barrier in the collinear *ab initio* potential energy surface should be 1.0−1.5 kcal/mole.

V. Conclusions

Calculations in support of a classical barrier height of 1.4±0.4 kcal/mole are presented. The bending potential near the saddle-point geometry is found to be very flat and to possess a slight minimum at noncollinear geometries. Since our best bending potential is in relatively good agreement with the SEC results of Schwenke *et al.* [8], it would be worthwhile to carry out quantum scattering calculations with this characteristic in the potential energy surface. A controversial point in the present theoretical calculations is the validity of applying a +Q correction for higher excitations to the CASSCF/MRCI calculations. Although this correction has no rigorous justification and is clearly an overcorrection when all important correlation effects can be included in the MRCI reference space, we believe that the +Q results are superior in this case and may well be an underestimate of the effects of higher excitations in the 9-electron treatments. This is based on FCI calibrations and in part on the belief that the full effect of the $2s$ correlation contribution to the barrier is only obtained at a very high level of correlation treatment.

The contention that the barrier is lower than previous theoretical calculations is also strongly supported by variational transition state theory calculations employing a surface computed with the CCI method. In agreement with previous work [6], the true bottleneck for the reaction is shifted considerably out into the entrance channel region as compared with the saddle-point geometry, where the combined zero-point and tunneling corrections are relatively small. Using the experimental thresholds [5] to reposition the computed barrier height favors a result in the lower half of the range 1.4±0.4 kcal/mole. Therefore, our work argues in favor of previous studies [7-9] that have recommended a relatively low barrier, and disagrees with the recent contention [3,4] that the barrier could not be less than 2.35 kcal/mole.

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Table I. FCI calibration of the classical barrier height[a].

A. At the FCI saddle point

	barrier	exothermicity
FCI[b]	4.50	28.84
MRCI(300)	5.18	28.57
MRCI(300)+Q	4.43	29.12
MRCI(322)(0.05)	5.00	29.12
MRCI(322)(0.05)+Q	4.32	29.21
MRCI(322)(0.025)	4.73	29.17
MRCI(322)(0.025)+Q	4.51	28.80
MRCI(322)(0.01)	4.71	29.19
MRCI(322)(0.01)+Q	4.54	28.84
MRCI(522)(0.025)	4.55	29.41
MRCI(522)(0.025)+Q	4.32	29.31

B. At optimized saddle-point geometry[c]

	r(F-H)	r(H-H)	barrier	exothermicity
FCI[b]	2.761	1.467	4.50	28.84
CPF[b]	2.801	1.467	4.40	26.47
MRCI(300)	2.740	1.476	5.16	28.57
MRCI(300)+Q	2.795	1.467	4.42	29.12
MRCI(311)[b]	2.722	1.473	5.15	28.68
MRCI(311)+Q[b]	2.773	1.464	4.39	29.21
MRCI(322)(0.025)	2.761	1.474	4.70	29.17
MRCI(322)(0.025)+Q	2.755	1.475	4.49	28.80

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[a] Energies in kcal/mole and bond lengths in a_0. All calculations are done using the [4s3p1d/2s1p] basis set and correlating 7 electrons. The barrier is referenced to F...H_2($50a_0$), and the exothermicity is computed using HF...H($50a_0$).

[b] Taken from Ref. 25 (FCI).

[c] Geometry optimizations were done using a biquadratic fit to a grid of nine points.

Table II. Spectroscopic constants for the $H_2(^1\Sigma_g^+)$ and $HF(^1\Sigma^+)$ systems, and basis set superposition errors.

	H_2	
	$r_e(a_o)$	$D_e(eV)$
SDCI	1.402	4.747
Expt[a]	1.401	4.747
	HF	
	$r_e(a_o)$	$D_e(eV)$
MRCI(200)	1.731	5.975
MRCI(200)+Q	1.735	6.057
MRCI(222)	1.735	6.064
MRCI(222)+Q	1.736	6.070
Expt[a]	1.733	6.123
	Superposition errors in kcal/mole[b]	
$H_2(F)$–SDCI[c]	0.01	
$F(H_2)$–SDCI	0.15(0.16)	
$F(H_2)$–MRCI(122)	0.15(0.16)	
$F^-(H_2)$–SDCI	0.58(0.65)	
$F^-(H_2)$–MRCI(222)	0.73(0.78)	
$F(H_2)$–SDCI(2p)	0.06(0.07)	
$F^-(H_2)$–SDCI(2p)	0.42(0.44)	
F(H)–SDCI(STO)[d]	0.35	

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[a] Ref. 27.

[b] The MRCI(300)+Q saddle point geometry is used, r(F-H)=2.921 and r(H-H)=1.450. The values in parentheses include a +Q correction.

[c] The nomenclature X(Y) denotes that X is computed with the Y ghost basis.

[d] The Slater basis set is taken from Ref. 2.

Table III. Theoretical studies of the classical saddle-point geometry and barrier for the F+H_2 reaction.

Basis[a]	Level of treatment	saddle-point		barrier[b]	exothermicity[b]
A	MRCI(300)	2.793	1.465	3.47	30.35
A	MRCI(300)+Q	2.921	1.450	2.29	31.00
Slater	MRCI(300)	2.80	1.46	3.24	
A	MRCI(322)	2.914	1.451	2.63	31.61
A	MRCI(322)+Q	2.950	1.450	1.66	30.47
A	MRCI(322)(2p)[c]	2.899	1.455	2.99	33.96
A	MRCI(322)(2p)+Q[c]	2.910	1.456	2.42	33.42
A	SDCI+Q	2.638	1.470	3.87	29.40
A	CPF	2.939	1.451	2.44	28.85
A	CCI(322)	...[d]	...[d]	2.79	31.8
A	CCI(322)+Q	...[d]	...[d]	2.02	30.7
A+H(*f*)[e]	CCI(322)	...[d]	...[d]	2.73	
A+H(*f*)	CCI(322) +Q	...[d]	...[d]	1.95	
A−F(*g*)	CCI(322)	2.879	1.447	2.89	
A−F(*g*)	CCI(322)+Q	2.909	1.445	2.14	
	Expt.				31.73

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[a] This letter "A" denotes the $[5s5p3d2f1g/4s3p2d]$ basis described in the text. The Slater basis is taken from Ref. 2.

[b] The barrier is referenced to F...$H_2(50a_0)$, and the exothermicity is computed using HF...$H(50a_0)$.

[c] These are 7-electron treatments (i.e. 2*s* correlation is excluded).

[d] The MRCI(300)+Q saddle point geometry is used, r(F-H)=2.921 and r(H-H)=1.450.

[e] Denotes that a function of this angular momentum type has been added.

Table IV. Zero-point and tunneling effects on the barrier height of the F + H_2 and F + D_2 reactions.

F + H_2 surface

	Classical Barrier		Adiabatic Barrier	
	CCI	CCI + Q	CCI	CCI + Q
r_{HF}, a_0	2.879	2.909	3.070	3.155
r_{HH}, a_0	1.447	1.445	1.425	1.421
Barrier, kcal/mole	2.888	2.143	2.639	1.860
Sym. stretch, cm^{-1}	3706	3768	4074	4178
Bend, cm^{-1}	68.5	45.9	68.5	45.9
Asym. stretch[a], cm^{-1}	$692i$	$605i$	$530i$	$371i$
Zero-point correction[b], kcal/mole	−0.602	−0.643	−0.076	−0.057
E barrier + zero point, kcal/mole	2.286	1.500	2.563	1.803
Tunneling correction, kcal/mole	−0.54	−0.47	−0.42	−0.29
Threshold, kcal/mole	1.75	1.03	2.14	1.51

F + D_2 surface

	Classical Barrier		Adiabatic Barrier	
	CCI	CCI + Q	CCI	CCI + Q
r_{HF}, a_0	2.879	2.909	3.010	3.075
r_{HH}, a_0	1.447	1.445	1.430	1.427
Barrier, kcal/mole	2.888	2.143	2.761	1.997
Sym. stretch, cm^{-1}	2623	2667	2811	2876
Bend, cm^{-1}	37.7	19.1	37.7	19.1
Asym. stretch[a], cm^{-1}	$512i$	$448i$	$428i$	$334i$
Zero-point correction[b], kcal/mole	−0.488	−0.532	−0.220	−0.233
E barrier + zero point, kcal/mole	2.400	1.611	2.541	1.764
Tunneling correction, kcal/mole	−0.40	−0.35	−0.34	−0.26
Threshold, kcal/mole	2.00	1.26	2.20	1.50

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[a] From the normal mode analysis at the classical barrier, and computed from the curvature along the Eckart potential at the adiabatic barrier.

[b] For $H_2(D_2)$ we used ω_e=4401(3116) cm^{-1}, respectively, from Ref. 26.

Figure Captions

Figure 1: CCI bending potentials for $F+H_2$, where $\theta=0$ corresponds to collinear approach. The bending curves are denoted by the CASSCF active space in C_s symmetry notation. The energy zero is arbitrary, but the curves are postioned relative to each other on the basis of total energy.

Figure 2: The CCI(82)+Q bending potential with respect to the reactants asymptote showing the first few vibrational levels for $F+H_2$ (solid lines) and $F+D_2$ (dashed lines). Vibrational energies with respect to the bending potential at $\theta=0$ are given in cm^{-1}.

Figure 3: Eckart potentials fit to the CCI+Q data for the classical potential along the minimum energy path (MEP) and for the adiabatic ground-state potential energy curves for $F+H_2$ and $F+D_2$. Values of the reaction coordinate s and r_{HF} are both given on the abscissa. The symbols represent the corresponding curves computed using the bicubic fit to the *ab initio* potential energy grid. All curves are relative to the energy of the reactants.