The Transition State of the F + H₂ Reaction

David E. Manolopoulos, Klaus Stark, Hans-Joachim Werner, Don W. Arnold, Stephen E. Bradforth, Daniel M. Neumark

The transition state region of the F + H₂ reaction has been studied by photoelectron spectroscopy of FH⁻. New para and normal FH⁻ photoelectron spectra have been measured in refined experiments and are compared here with exact three-dimensional quantum reactive scattering simulations that use an accurate new ab initio potential energy surface for F + H₂. The detailed agreement that is obtained between this fully ab initio theory and experiment is unprecedented for the F + H₂ reaction and suggests that the transition state region of the F + H₂ potential energy surface has finally been understood quantitatively.

The transition state plays a central role in chemical reaction dynamics (1). Asymptotically observable quantities such as integral cross sections and thermal rate constants often depend crucially on what happens in a relatively narrow region around the transition state saddle point, and a number of approximate and exact theories of bimolecular reaction reactions exploit this (2). It is therefore particularly interesting if an experiment can be devised to look directly at the transition state, without having to infer what happens there from asymptotic measurements. The photoelectron spectroscopy of stable negative ions such as FH⁻ is one such experiment that has been developed recently at Berkeley (3). In favorable circumstances, when the equilibrium geometry of the anion lies close to the neutral transition state, the photoelectron spectrum of the anion can give a direct vibrationally resolved picture of the transition state dynamics and so realize the goal of “transition state spectroscopy.”

The circumstances are particularly favorable for FH⁻, which photodetaches close to the transition state of one of the most thoroughly investigated reactions in chemical dynamics. Various aspects of the (asymptotic) product energy and angular distributions of the F + H₂ reaction have been measured in chemical laser (4), infrared chemiluminescence (5), and crossed molecular beam experiments (6), for example, and accurate thermal rate constants have been obtained over a large temperature range (7). The reaction has also played a key role in the development of quantum reactive scattering theory, with its high exoergicity, unsymmetrical mass combination, pronounced resonance structure, and experimental accessibility all making it a prime target for study (8). Moreover, the challenges posed by the transition state region of the F + H₂ potential energy surface (PES) have long made it a favorite problem in electronic structure theory (9), and numerous global F + H₂ potential energy functions have been proposed (10, 11).

Given this background and encouraging early work on the FH⁻ system by Zhang and Miller (12) and Weaver and Neumark (13), four of the present authors have recently completed a detailed experimental and theoretical study of the FH⁻ photoelectron spectrum (14). Experiments were performed in this study for both para and normal FH⁻, that is FH⁻ ions prepared by clustering F⁻ with both para and normal hydrogen, and three previously proposed semiempirical F + H₂ PESs (11) were used in quantum mechanical simulations of the resulting spectra. (Recall that in para H₂ only the even rotational levels are populated, whereas in normal H₂ the odd/even population ratio is 3:1.) The study succeeded in showing that the para and normal FH⁻ photoelectron spectra are dominated by bending progressions associated with the F + H₂ transition state region and are therefore highly sensitive to the details of the F + H₂ bending potential in this region. None of the three F + H₂ PESs used in the quantum dynamics simulations was particularly successful, however, in giving a truly quantitative prediction of the experimental spectra (14).

The inadequacies of the semiempirical surfaces suggest that a better approach is to construct a fully ab initio PES for F + H₂, which has proved a considerable challenge. The main problem is that both the classical barrier height and the bending potential at the transition state are highly sensitive to electron correlation, and very large orbital and configuration basis sets are required if they are to be converged to chemical accuracy (9, 15, 16). However, a recent benchmark full configuration interaction (CI) calculation by Knowles et al. (15) and systematic studies of the convergence of the topology of the FH⁻ transition state with respect to the orbital basis and electron correlation treatment (16) have shown that the barrier height and reaction exothermicity can now be obtained to sufficient accuracy for dynamics calculations. Calculations at this level of convergence are highly sophisticated and require the use of very large orbital basis sets, extended internally contracted multireference CI (MRCl) wave functions (17) with complete active space self-consistent field (CASSCF) reference functions (18), and application of the Davidson correction (19) for the effect of higher excitations (MRCl + Q). Nevertheless, because the barrier height and reaction exothermicity are sensitive to very different regions of the PES and yet are obtained with comparable (0.1 kcal/mol) accuracy (15, 16), and because the MRCl + Q calculations are efficient enough to be performed at a large number (≈600) of other geometries, a globally accurate F + H₂ PES is promised by this same level of theory. Such a highly correlated ab initio PES for F + H₂ has recently been constructed by two of the present authors (16), and the remainder of this report provides the first stringent experimental test of this new surface by comparison with the para and normal FH⁻ photoelectron spectra.

A two-dimensional cut through the transition state region of the new F + H₂ PES as a contour diagram is shown in Fig. 1, with contours of the para FH⁻ vibrational ground state wave function superimposed. The anion wave function is calculated in the harmonic normal mode approximation (12) and the best available equilibrium geometry (R(FH⁻) = 2.075 Å, R(F-H) = 0.770 Å, and v = 0) and vibrational frequencies (ω₁ = 292 cm⁻¹, ω₂ = 773 cm⁻¹, and ω₃ = 4143 cm⁻¹) from the ab initio calculations of Nichols et al. (20) are used. The corresponding ortho wave function may be obtained by reversing the sign of one of the two lobes and is degenerate with the para wave function in Fig. 1 (14, 16).

The key features of the para and normal FH⁻ photoelectron spectra are already implicit in Fig. 1. The first thing to notice is that the anion wave function has a good
Franck-Condon overlap with the neutral transition state, as has already been mentioned above. The \( \text{FH}_2^- \) equilibrium geometry given by Nichols et al. is linear with \( \text{F-H} \) and \( \text{H-H} \) distances of 1.690 and 0.770 Å (20), for example, and the corresponding distances at the two degenerate saddle points on the \( \text{F} + \text{H}_2 \) surface are similar at 1.541 and 0.772 Å (15). Indeed, the fact that the \( \text{H-H} \) bond length changes so little from the anion to the neutral in the Franck-Condon region is what allows us to eliminate this coordinate from Fig. 1 without losing any essential information. The physical implication of the small \( \text{H-H} \) bond length change is minimal \( \text{H}_2 \) vibrational excitation on photodetachment (see below).

The second thing to notice about Fig. 1 is that, in contrast to the linear equilibrium geometry of the anion, the saddle points on the new \( \text{F} + \text{H}_2 \) surface are bent at an \( \text{F-H-H} \) bond angle of 119° (15). The coordinate which experiences the largest change in potential energy on photodetachment is therefore a bending coordinate, which explains why the observed \( \text{FH}_2^- \) photoelectron spectra are dominated by bending progressions (14). It also explains why the \( \text{para} \) and \( \text{normal} \) \( \text{FH}_2^- \) photoelectron spectra are so different, with the former only containing transitions to bending states that correlate asymmetrically with \( \text{F} + \text{H}_2 \) (even \( j \)) and the latter containing transitions to states that correlate with both \( \text{F} + \text{H}_2 \) (odd \( j \)) and \( \text{F} + \text{H}_2 \) (even \( j \)) in the usual 3:1 \( \text{ortho} : \text{para} \) ratio.

According to the model developed by Schatz (21), and adapted for the present problem by Zhang and Miller (12), the \( \text{FH}_2^- \) photoelectron spectrum can be simulated quantum mechanically through the calculation of a simple Franck-Condon factor:

\[
P(E) = \sum_n |\langle \Psi_n(E) | \Psi \rangle|^2
\]

Here \( \Psi_n(E) \) is an energy-normalized \( \text{F} + \text{H}_2 \) reactive scattering wave function at energy \( E \) with asymptotic quantum numbers \( n \), and \( \Psi \) is the initial rovibrational wave function of the anion. In practice, the permutation symmetry of the two hydrogens can be exploited to reduce Eq. 1 to two separate Franck-Condon factors, one each for \( \text{ortho} \) and \( \text{para} \), and these can then be combined in the appropriate ratio to simulate the \( \text{normal} \) \( \text{FH}_2^- \) spectrum (14). The use of this model to simulate an anion photoelectron spectrum involves several fundamental assumptions, including in particular the assumption that the transition moment \( \mu_g \) for the electronic transition is a constant function of both the nuclear coordinates in the Franck-Condon region and the scattering energy \( E \) of the neutral photofragments (22). However, the results presented below suggest that these assumptions are justified for \( \text{FH}_2^- \).

Theoretical simulations of the \( \text{para} \) and \( \text{normal} \) \( \text{FH}_2^- \) photoelectron spectra have been performed on the new \( \text{F} + \text{H}_2 \) surface by using an exact quantum reactive scattering method by Schatz (23) for calculating the reactive scattering wave functions in Eq. 1 in conjunction with the harmonic normal mode approximation for the anion. Full three-dimensional quantum reactive scattering calculations such as these have only become possible quite recently as a result of a revolution in computational methodology (24). However, the present anion photoelectron spectrum simulations are comparatively straightforward because only a few angular momentum states of the (rotationally cold) anion are expected to be populated in the experiment. This means that only a few partial waves of the neutral reaction contribute, and \( J = 0 \) provides a good approximation to the full spectrum. Therefore, in addition to being particularly sensitive to the transition state region and largely immune to the angular momentum averaging that washes dynamical structure out of more conventional full-collision measurements (25), the \( \text{FH}_2^- \) photoelectron spectrum provides a probe of the \( \text{F} + \text{H}_2 \) PES that is computationally very accessible.

Fig. 1. The transition state region of the \( \text{F} + \text{H}_2 \) PES and its overlap with the \( \text{FH}_2^- \) anion wave function. The solid lines are contours of the new \( \text{F} + \text{H}_2 \) PES in steps of 0.4 kcal/mol from 0.4 to 2.8 kcal/mol, relative to the bottom of the asymptotic \( \text{F} + \text{H}_2 \) valley. The long dashed lines are similar contours from -2.8 to 0.0 kcal/mol. The short dashed lines are contours of the \( \text{para} \) \( \text{FH}_2^- \) anion wave function, each successive contour representing a decrease in the square modulus of the wave function by a factor of 10. The coordinates of the plot are the \( \text{F-H} \) distance \( R \) and the Jacobi angle \( \gamma \) that are illustrated in the inset; the \( \text{H-H} \) bond length \( r \) is fixed at 0.771 Å throughout (see text). The \( \text{F} + \text{H}_2 \) transition state saddle points (S) occur along minimum potential energy paths between a \( \text{C}_2v \) symmetry van der Waals well in the \( \text{F} + \text{H}_2 \) reagent valley and the two degenerate \( \text{H} + \text{HF} \) product valleys.

Fig. 2. Comparison between experimental (solid line) and theoretical (dashed line) \( \text{FH}_2^- \) photoelectron spectra: (A) \( \text{para} \) \( \text{FH}_2^- \) and (B) \( \text{normal} \) \( \text{FH}_2^- \). The experimental spectra were obtained in refined experiments as described in the text. The theoretical spectra were obtained from Eqs. 1 and 2 by performing exact three-dimensional quantum reactive scattering calculations on the new \( \text{F} + \text{H}_2 \) PES and convoluting the resulting \( P(E) \)s with a Gaussian (19 meV full-width at half-maximum) to approximate the experimental resolution in the neighborhood of the dominant peaks.

\[
eKE = h\nu - D_0(\text{FH}_2^-) - \text{EA}(\text{F}) + \text{ZPE}(\text{H}_2) - E
\]
In Fig. 2, $D_0$ has been adjusted to align the main peaks in the simulated and experimental para FH$_2^-$ spectra, giving $D_0 = 0.205$ eV, and the same relation between eKE and $E$ has been used for normal FH$_2^-$.

Theoretical spectra have also been convoluted with a Gaussian (full-width at half-maximum of 19 meV) to approximate the experimental resolution at eKE = 1.0 eV.

The new experimental spectra in Fig. 2 were obtained with the same apparatus as described previously (14), with photoelectrons collected parallel to the electric field vector of the (plane polarized) photodetachment laser so as to minimize the contribution from excited F + H$_2$ electronic states (13). However, both spectra have been significantly improved. In particular, the contribution from excited F + H$_2$ electronic states has been further reduced by improving the purity of the laser polarization. The effect of this improved polarization is well illustrated by the region eKE < 0.8 eV, where the photoelectron signals are close to baseline in both spectra; this is precisely the region in which transitions to excited F + H$_2$ electronic states are expected to be most pronounced (14).

Another more important modification was also used to obtain the para FH$_2^-$ spectrum in Fig. 2A. The experimental para FH$_2^-$ spectrum shown in our earlier paper consisted of a broad central feature with some partially resolved features on either side (14), whereas considerably more structure was found in the simulations. We postulated that the experimental spectrum was likely to be contaminated by a certain amount of para \( \rightarrow \) ortho conversion on the walls of the gas mixing cylinder prior to the experiment, and the evidence for this was made even stronger by the present theoretical calculations. The spectrum shown in Fig. 2A was therefore obtained in a new experiment prior to which the NF$_2$ / para H$_2$ mixture was held in an aluminum (rather than stainless steel) gas cylinder so as to reduce the conversion. The effect of this final modification was found to be quite dramatic, and indeed the experimental para FH$_2^-$ spectrum in Fig. 2A shows three pronounced peaks between eKEs of 0.8 and 1.1 eV. This improvement allows a considerably more detailed comparison with theory than was possible with the earlier data.

The assignment of the FH$_2^-$ photoelectron spectra in Fig. 2 is similar to that deduced in our earlier paper from simulations on other F + H$_2$ PESs (14). Thus, the two peaks in the para FH$_2^-$ spectrum in Fig. 2A at eKE = 0.974 and 0.877 eV are transitions to FH$_2^-(j)$ bending (or hindered rotor) states with quantum numbers $j = 2$ and 4, in order of decreasing eKE (see Eq. 2). A one-dimensional bending simulation (14) on the new F + H$_2$ PES reveals that the FH$_2^-(j = 0)$ peak occurs with low intensity just above eKE = 1.0 eV, but this peak is not really discernable in either the three-dimensional simulations or the experiment. The three peaks in the normal FH$_2^-$ spectrum in Fig. 2B at eKE = 0.993, 0.943, and 0.815 eV are transitions to FH$_2^-(j)$ hindered rotor states with quantum numbers $j = 1$, 3, and 5. These ortho peaks are more apparent than the para peaks because of the 3:1 ortho:para ratio. The small peaks at eKE = 0.5 eV in both spectra are transitions to FH$_2^-$ states that correlate with vibrationally excited H$_2$($v = 1$); the fact that these peaks are not so pronounced in the theoretical simulations suggests that the harmonic normal mode approximation may be somewhat inadequate for the anion, and requires further investigation. Finally, the narrow peak in the para FH$_2^-$ spectrum at eKE = 1.044 eV is due to a scattering resonance associated with a quasi-bound state in the H + HF product valley. In contrast to the pure bending states of the F + H$_2$ transition state, which are restricted by symmetry to either para or ortho FH$_2^-$, this resonance contribution shows up at the same scattering energy (between $E = 0.280$ and 0.285 eV) in both simulations. It is therefore particularly pleasing that it is also seen in the improved experimental normal FH$_2^-$ spectrum as a small bump on the shoulder of the FH$_2^-(j = 1)$ peak at eKE = 1.035 eV. These assignments are summarized in Table 1.

Table 1. Assignment of peaks in the FH$_2^-$ photoelectron spectra (Fig. 2).

<table>
<thead>
<tr>
<th>Peak position (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.044</td>
<td>H/2HF resonance</td>
</tr>
<tr>
<td>0.974</td>
<td>F/H$_2$($v = 0$, $j = 2$)</td>
</tr>
<tr>
<td>0.877</td>
<td>F/H$_2$($v = 0$, $j = 4$)</td>
</tr>
<tr>
<td>0.943</td>
<td>F/H$_2$($v = 1$)</td>
</tr>
<tr>
<td>0.815</td>
<td>H/2HF resonance</td>
</tr>
<tr>
<td>0.904</td>
<td>F/H$_2$($v = 0$, $j = 1$)</td>
</tr>
<tr>
<td>0.943</td>
<td>F/H$_2$($v = 0$, $j = 3$)</td>
</tr>
<tr>
<td>0.815</td>
<td>F/H$_2$($v = 0$, $j = 5$)</td>
</tr>
<tr>
<td>0.5</td>
<td>F/H$_2$($v = 1$)</td>
</tr>
</tbody>
</table>

*Shoulder.*

The improvement in the theoretical spectra is attributable solely to the improved accuracy of the present ab initio F + H$_2$ surface in the transition state region, because our earlier simulations used the same harmonic normal mode parameters for FH$_2^-$.

Thus, the present combination of ab initio electronic structure theory, ab initio quantum dynamics, and a novel transition state spectroscopy experiment would appear finally to have converged on an accurate description of the F + H$_2$ transition state region.

It will be interesting in future work to see whether the agreement between theory and experiment in Fig. 2 can be made even better by going beyond the harmonic normal mode approximation to the FH$_2^-$ anion, which is probably the largest single approximation in the present model. It will also be interesting to see whether the present F + H$_2$ PES gives a good quantitative prediction of the asymptotic experimental properties of the F + H$_2$ reaction, such as the HF product vibrational branching ratio and angular distributions (4–6). These properties provide a sensitive probe of the PES in the H + HF product valley and so are somewhat complementary to the transition state spectroscopy measurements considered here.

REFERENCES AND NOTES

1. For example, see Faraday Discuss. Chem. Soc. 81, 1 (1991).
Nitrogen-15 and Oxygen-18 Characteristics of Nitrous Oxide: A Global Perspective

K.-R. Kim* and H. Craig

The global budget of N₂O shows a significant imbalance between the known rate of destruction in the stratosphere and the estimated rates of natural and anthropogenic production in soils and the ocean. Measurements of the ¹⁵N/¹⁴N and ¹⁸O/¹⁶O ratios in two major tropospheric sources of N₂O, tropical rain forest soils and fertilized soils, show that soil N₂O from a tropical rain forest in Costa Rica and from sugar-cane fields in Maui is strongly depleted in both ¹⁵N and ¹⁸O relative to mean tropospheric N₂O. A major source of heavy N₂O, enriched in both ¹⁵N and ¹⁸O, must therefore be present to balance the light N₂O from soils. One such source is the back-mixing flux of N₂O from the stratosphere, which is enriched in ¹⁵N and ¹⁸O by photolysis and chemistry. However these return fluxes of ¹⁵N and ¹⁸O are so great that a large oceanic flux of N₂O is required to balance the heavy isotope–enriched stratospheric flux. All these effects will be reflected in climatically related isotopic variations in trapped N₂O in polar ice cores.

Nitrogen oxide (N₂O) is an active atmospheric trace gas (tropospheric mixing ratio = 310 ppbv) that is currently increasing in concentration at a rate of ~0.25% per year (1). Various sources both natural and anthropogenic have been identified, but the relative importance of these sources has not yet been established, although it seems clear that tropical forest soils are the primary single source (2, 3). The atmospheric residence time of N₂O relative to destruction by stratospheric photolysis and chemistry is ~150 years, but known and estimated inputs to the atmosphere are only about half of the flux required to balance the calculated destruction rate (4), and reasons for the imbalance are unknown.

Characterization of tropospheric and dissolved oceanic N₂O by the two isotope ratios ¹⁵N/¹⁴N and ¹⁸O/¹⁶O provides important constraints on the geochemistry and sources of this gas (5). In this report we extend this approach to a study of N₂O in tropical rain forest soils (6) and in stratospheric air. The ¹⁵N/¹⁴N and ¹⁸O/¹⁶O ratios were measured by injecting molecular N₂O directly into the dual-inlet, triple-collecting mass spectrometer SAMSON and simultaneously measuring masses 44, 45, and 46 for the ¹⁵N/¹⁴N and ¹⁸O/¹⁶O isotope ratios (7).

Soil-gas samples were collected from natural soils in the rain forest of Costa Rica (8, 9) and from fertilizer-treated soils of sugar-cane fields on the island of Maui (10). Air samples were withdrawn from existing soil-flux measurement chambers (11) and returned to La Jolla where the N₂O-air mixing ratios were determined by ECD gas chromatography, and the isotope ratios were measured. Table 1 shows that quasi-duplicate samples at one Maui site and at one of the Costa Rican sites agree quite well for both the measured N₂O mixing ratios and the end-member isotopic δ values of the soil N₂O (12).

Figure 1 shows the soil-N₂O isotopic data and the δ values of tropospheric N₂O (5). Although the isotopic values from different soil sites show rather large variations, they are uniformly depleted in the heavy isotopes and isotopically lighter than the tropospheric air and oceanic samples in all cases. On Maui N₂O from the abundant rainfall site is enriched in the heavy isotopes of both N and O relative to N₂O from the dry-side soil. This effect may be due to denitrification in the wet soils, as nitrification in dry soils generally produces isotopically light N₂O (13, 14).

These data show that the isotopic ratios of N₂O emitted from soils in both the natural and fertilized states are significantly depleted in ¹⁵N and ¹⁸O relative to tropospheric N₂O. Thus there must also exist sources of N₂O enriched in the heavy isotopes to balance the input fluxes of light soil-gas N₂O.

One such heavy tropospheric source is the N₂O produced by nitrification in deep ocean water (5); these data are also plotted in Fig. 1. The heavy isotope enrichments in these waters increase with depth, but the deep-water production is not a significant tropospheric source. In contrast to these heavy isotope–enriched samples, the δ values of near-surface dissolved N₂O are quite similar to those of tropospheric N₂O but are slightly depleted in ¹⁵N and ¹⁸O. It is possible that in some oceanic areas of strong regional upwelling such as the Equatorial Eastern Pacific (15) and the northwest Indian Ocean (16), N₂O brought to the surface may have been produced by denitrification (17) and that N₂O produced in this way may be enriched in ¹⁵N (18), and perhaps in ¹⁸O, relative to values for tropospheric air. However the δ values of dissolved N₂O in shallow depths (surface to depths of ~800 m) are quite similar to those of tropospheric N₂O (5), Fig. 1, so that there is a strong buffering effect of subsurface N₂O
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