QUANTUM EFFECTS IN THE F+H₂ \rightarrow HF+H REACTION. ACCURATE 3D CALCULATIONS WITH A REALISTIC POTENTIAL ENERGY SURFACE

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We report accurate benchmark 3D coupled channel calculations for total angular momentum J=0 for the reaction $F+H_2 \rightarrow HF+H$ using a realistic potential energy surface. The adiabatic basis functions are generated using the discrete variable representation method. The resulting reaction probabilities show what appear to be strong quantum resonance features as well as rapid changes in final rotational state distributions.

1. Introduction

As a prototypical highly excergic reaction, the HF laser reaction,

$$\mathbf{F} + \mathbf{H}_2 \to \mathbf{H}\mathbf{F} + \mathbf{H} \,, \tag{1}$$

continues to generate intense experimental and theoretical interest. In this Letter we will not attempt to review the many experiments on this system, but we do want to note the molecular beam experiments of Neumark et al. [1], which show clear evidence of quantum resonance effects: the vibrationally excited products HF(v) with v=3 appear at *all* scattering angles while all those with $v \le 2$ are strongly backward peaked at the energies of the scattering experiments.

We will also not attempt to review the many classical, collinear, and approximate 3D quantum calculations on this system. One coupled channel (CC) calculation in the full three-dimensional (3D) physical space has been reported for zero total angular momentum (J=0) by Zhang and Miller [2]. The resulting reaction probabilities show considerable interesting structure as a function of energy. However, Zhang and Miller used the Muckerman 5 po-

² Present, permanent address: Department of Physics and Astronomy, University of Oklahoma, Norman, OK 73019, USA. tential energy surface [3] which is known to have serious deficiencies, so that the significance of those structures to the real system is unclear.

The calculation of an accurate potential energy surface (PES) for this reaction continues to pose a challenge to quantum chemistry [4]. The PES used in the present work, which we denote by T5A to distinguish id from the M5 surface mentioned above, is surface 5A of Truhlar and coworkers (rcf. [5], as modified in ref. [6]). More recent ab initio calculations [7] indicate that the bending potential of this PES near the FHH transition state is not accurate, but this PES, which combines ab initio and empirical information, corrects most of the deficiencies of earlier surfaces and is the most accurate PES for which an analytic fit to the complete surface is available [8].

Until now, the most accurate calculations using the T5A PES have been the bending corrected rotating linear model (BCRLM) calculations of Hayes and Walker [9]. The resulting differential cross sections agreed much better with experiment [1] than previous calculations and provided plausible explanations for many, but not all, of the observed resonance effects.

In this Letter we report what we believe are the first accurate 3D converged full CC calculations for J=0 for this reaction using this realistic T5A PES. These calculations also represent our first application of the discrete variable representation (DVR)

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method to the calculation of the adiabatic surface function basis. The resulting reaction probabilities show a surprisingly rich structure with energy.

2. Theory and calculation

The present reactive scattering calculations use the adiabatically adjusting principal axes hyperspherical (APH) theory which has been detailed elsewhere [10,11]. This approach involves two steps: (1) calculation of a basis of adiabatic surface functions and (2) solution of the resulting CC scattering equations.

In the first step, the range of the APH hyperradius ρ is divided into sectors with the center of the ξ th sector at ρ_{ξ} . For each ρ_{ξ} , $\xi = 1, ..., n$, we solve for the eigenfunctions $\Phi(\theta, \chi; \rho_{\xi})$ of a two-dimensional Schrödinger equation in the hyperangles θ and γ . This is the most time consuming step of our calculations for two reasons. First, a large number (N) of surface functions Φ have to be calculated at each ρ_{F} for many values of ρ_{ξ} . (For F+H₂, we use up to N=150 for n=147 sectors.) Second, the shape and size of the potentials in θ and χ vary strongly as a function of ρ_{ξ} . For the calculations to be feasible, the method for determining surface functions must be: (1) fast, yet accurate; (2) capable of handling a wide range of complicated nonseparable 2D potentials; and (3) implemented in an essentially automatic fashion with respect to input parameters. We found the finite element method (FEM), which we use in our earlier calculations [9,10], to be too slow and too inaccurate for $F+H_{2}$.

Variational bound state methods based on the discrete variable representation (DVR) [12] have proven to be exceptionally efficient for calculating highly excited, large amplitude vibrational states of strongly coupled multidimensional systems with arbitrarily shaped potential surfaces [13,16]. Surface function calculations by Whitnell and Light [17] for $H+H_2$ and our preliminary work on $H+H_2$ and $F+H_2$ demonstrated that the DVR is currently the method of choice for obtaining surface functions. For $F+H_2$, the DVR gives solutions 5 times faster than the FEM where the former solutions are accurate and the latter are inaccurate.

Following Whitnell and Light [17], θ was discretized in the DVR consisting of Gauss-Legendre quadrature points, and a symmetry adapted DVR (SADVR) was used to discretize y. A SADVR [17] appropriate for the J=0 F+H₂ system, with C_{2v} symmetry, was defined by a set of functions $\cos[2(m-1)\chi]$. The surface functions were determined using the diagonalization-truncation procedure of Bačić et al. [18]. For each discrete value of θ , a one-dimensional ray Hamiltonian [13–16] in χ was diagonalized. The ray Hamiltonian was truncated by neglecting any DVR points where the value of the potential was greater than a cutoff value V_{max} . The full J=0 surface Hamiltonian matrix was then constructed in a truncated ray eigenvector basis. consisting of those 1D eigenvectors in χ with eigenvalues below a certain energy cutoff parameter E_{cut} . The relatively small size (<940) of the 2D DVR surface Hamiltonian matrices allowed us to efficiently solve for the full surface eigenstate spectrum by direct diagonalization.

The potential coupling matrix elements required for the CC calculations and the overlap matrices between surface functions belonging to neighboring sectors, necessary for transforming the **R** matrix from one sector to another [10], were also calculated efficiently in the 2D DVR. At ρ_m , the surface functions were transformed from the DVR to the finite basis function representation (FBR), so that they could be used to obtain the Delves **R** matrix from the APH **R** matrix [10]. Details of these DVR and FBR calculations will be given later [19].

The parameters used to generate the DVR surface functions are as follows. The corresponding FBR basis included the set of Legendre polynomials $\{P_l(\cos 2\theta)\}$ up through $l_{\max} = 50$ and the set of cosince in χ up through $m_{\text{max}} = 100$. The initial and final sector values were $\rho_1 = 2.2 a_0$ and $\rho_{147} = 9.405 a_0$, respectively (1 $a_0 = 1$ bohr radius). The 147 sectors were placed at the intervals $\rho_{\xi+1} = 1.01\rho_{\xi}$. The values of l_{max} and m_{max} were determined by converging the 100th surface function eigenvalue $\mathscr{E}_{l=100}(\rho) = 2.155$ eV to 4 figures at $\rho = 9.5 a_0$. Since the arrangement channels shrink in the θ , χ coordinate space as ρ increases, the resulting FBR basis set is more than adequate at the values of $\rho < 9.5 a_0$ as we have verified. $E_{\rm cut}$ was fixed at 4.0 eV between 4.028 and 9.405 a_0 for ρ_{ξ} . Between 2.2 and 4.028 a_0 , E_{cut} varied in a manner that kept E_{cut} about twice $\mathscr{E}_{100}(\rho_{\xi})$ at each ρ_{ξ} . We set $V_{\text{max}} = 1.75 E_{\text{cut}}$ at every value of ρ_{ξ} . We

have found from experience that these choices for $E_{\rm cut}$ and $V_{\rm max}$ provide $\mathscr{E}_{100}(\rho_{\xi})$ converged to 4 figures or more.

The exact CC equations (coupled in the adiabatic basis) were propagated from ρ_1 to ρ_{147} using the logderivative method [20], and the boundary conditions were applied as usual [10]. The calculations presented are converged with respect to the number of propagation steps in each sector.

The surface functions, matrix elements, and overlaps were calculated on an Ardent TITAN superminicomputer. The CC equations were propagated on a CRAY-XMP 4/16 supercomputer.

3. Results

In table 1 we present a convergence study of the distinguishable particle reaction probabilities as a function of the number of adiabatic surface functions N. $P_{00}^{R}(v_{f}, j_{f})$ is the reaction probability from the initial H₂ rovibrational state ($v_{i}=0, j_{i}=0$) into both HF arrangement channels of final state (v_{f}, j_{f}). Reaction probability summed over all open rotational states within a given v_{f} vibrational manifold is

$$P_{00}^{\mathsf{R}}(v_{\mathsf{f}}) = \sum_{j_{\mathsf{f}}} P_{00}^{\mathsf{R}}(v_{\mathsf{f}}, j_{\mathsf{f}}) .$$
 (2)

We also consider the total reactivity out of initial state $(v_i=0, j_i=0)$ which is also summed over all open vibrational channels,

$$P_{00}^{\rm R}(\text{total}) = \sum_{v_{\rm f}} P_{00}^{\rm R}(v_{\rm f}) .$$
(3)

Although we report three figures in table 1 for comparative purposes, the $P_{00}^{R}(v_{f})$ are only certain to about two significant figures. The total energy (internal plus translational) is measured from the bottom of the asymptotic HF well. The 0.1 eV energy intervals in table 1 provide a representative sampling of the convergence behavior. Also, we have provided results at smaller intervals around the region where $v_{f}=4$ becomes energetically open (2.092 eV). At 2.10 eV, just above the $v_{f}=4$ threshold, the probabilities appear to be very sensitive with respect to varying N, whereas the probabilities at energies on both sides of 2.10 eV are better converged. The P_{00}^{R} (total) appears converged to better than 2% except at 2.10 eV where it is converged to about 3%. At 2.10 eV $P_{00}^{R}(4)$ is only converged to within 18% whereas at 2.40 eV it is converged to within 2%. Convergence is usually slower at higher energy because more states are open, but the present behavior is due to increased sensitivity in the $v_{\rm f}$ =4 threshold region where the probabilities are varying rapidly. The $P_{00}^{R}(3)$ are all converged to within about 2% as are all of the $P_{00}^{R}(2)$ except at 2.40 eV where the convergence is within 5%. The $P_{00}^{R}(1)$ and $P_{00}^{R}(0)$ are relatively small (no greater than 0.03 and 0.0005, respectively) yet are all converged to better than 8% and 15%, respectively.

To compare with calculations which use asymptotic basis functions we provide the asymptotic correlation of the adiabatic bases used. For transitions out of H₂ initial states with even j only surface functions which correlate with even *j* are needed in the H₂ arrangement due to symmetry whereas surface functions which correlate with all j are needed in the HF arrangements. The notation $(j_0, j_1, ..., j_n)$ denotes the highest i state included within the v vibrational manifold. These correlations are: for N=150, H₂ channels = (12, 8, 2) and HF channels = (31, 28, 24, 32)21, 16, 10); for N = 140, $H_2 = (10, 6)$ and HF = (30, 6)27, 24, 20, 15, 8); and for N=129, $H_2=(10, 6)$ and HF = (29, 26, 23, 18, 13, 4). Since our basis functions are determined adiabatically, they provide a better basis than a strictly asymptotic basis containing the same number of functions.

In fig. 1 we show distinguishable particle reaction probabilities as a function of total energy for the F+H₂ reaction on the T5A PES for J=0. There are a total of 95 scattering energies, and N=150 adiabatic basis functions were included. The S matrices were unitary to a part per thousand or better even at the highest energy. We note that the most striking aspect of fig. 1 is that the P_{00}^{R} (total) as well as the $P_{00}^{R}(v_{f})$ for the individual vibrational channels show much structure and vary rapidly over many regions of energy.

In an attempt to clarify some of the observed structure in fig. 1, we have also plotted HF final rovibrational state reaction probability $(P_{00}^{R}(v_{f}, j_{f}))$ distributions in fig. 2 as a function of j_{f} for $v_{f}=2$ and 3 at three total energies. Figs. 2a-2c, obtained at 1.78,

Total	$P_{00}^{\mathbf{R}}(\nu_{\mathrm{f}}=0)$			$P_{00}^{\rm R}(v_{\rm f}=1)$			$P_{00}^{\rm R}(v_{\rm f}=2)$		
energy " (eV)	$N^{b} = 129$	N = 140	<i>N</i> =150	<i>N</i> =129	<i>N</i> =140	<i>N</i> =150	<i>N</i> =129	N = 140	<i>N</i> =150
1 70	0.262(_5) 0)	0.215(-5)	0.221(-5)	0.594(-3)	0.577(-3)	0.570(-3)	0.614(-1)	0.616(-1)	0.611(-1)
1 80	0.601(-4)	(-4)	0.630(-4)	0.780(-2)	0.788(-2)	0.792(-2)	0.117	0.118	0.118
1.90	0.125(-3)	0.131(-3)	0.129(-3)	0.907(-2)	0.903(-2)	0.896(-2)	0.104	0.104	0.104
2.00	0.312(-3)	0.351(-3)	0.340(-3)	0.210(-1)	0.213(-1)	0.212(-1)	0.164	0.162	0.164
2.10	0.304(-3)	0.280(-3)	0.332(-3)	0.172(-1)	0.163(-1)	0.164(-1)	0.144	0.142	0.143
2.20	0.462(-3)	0.433(-3)	0.420(-3)	0.176(-1)	0.167(-1)	0.157(-1)	0.128	0.127	0.126
2.30	(p –	0.384(-3)	0.444(-3)	1	0.141(-1)	0.143(-1)	I	0.121	0.120
2.40	I	0.416(-3)	0.401(-3)	I	0.122(-1)	0.113(-1)	1	0.113	0.108
	$P_{00}^{R}(v_{f}=3)$			$P_{00}^{\rm R}(v_{\rm f}\!=\!4)$			$P_{00}^{\rm R}$ (total)		
	<i>N</i> =129	N=140	<i>N</i> =140	N=129	N = 140	N = 150	<i>N</i> =129	N = 140	<i>N</i> =150
1.70	0.278	0.279	0.280	0.0	0.0	0.0	0.340	0.341	0.341
1.80	0.391	0.392	0.392	0.0	0.0	0.0	0.516	0.518	0.518
1.90	0.609	0.611	0.610	0.0	0.0	0.0	0.722	0.724	0.723
2.00	0.446	0.454	0.450	0.0	0.0	0.0	0.632	0.638	0.635
2.04	I	0.384	0.383	0.0	0.0	0.0	ı	0.655	0.657
2.08	1	0.591	0.581	0.0	0.0	0.0	ı	0.723	0.713
2.10	0.392	0.424	0.419	0.151	0.103	0.125	0.404	0.685	0.704
2.12	ı	0.437	0.438	ı	0.124	0.117	1	0.706	0.699
2.16	I	0.356	0.351	1	0.862(-1)	0.939(-1)	I	0.595	0.599
2.20	0.421	0.430	0.431	0.160	0.174	0.168	0.727	0.747	0.741
2.30	1	0.384	0.391	ļ	0.134	0.135	I	0.653	0.660
2.40	1	0.421	0.430	I	0.185	0.182		0.732	0.732

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0.20

0.15

0.10

(a)

20

(b)

(c)

16 18

14

E=1.78 eV

12

12 14 16 18 20

12 14 16 18 20



Fig. 1. $\mathbf{F} + \mathbf{H}_2$ reaction probabilities $P_{00}^{\mathbf{R}}(v_f)$ for J=0 plotted versus total energy. Legend (listed in order from smallest to largest P_{00}^{R} at total energy = 2.20 eV): (diamond), v_{f} = 1; (asterisk), v_{f} = 2; (dot), $v_f=4$; (open circle), $v_f=3$; \times , total reactivity. The points are connected for clarity. $v_r = 0$ is not shown as it is negligible on this scale (see table 1).

1.82, and 1.86 eV, respectively, are representative of the lowest energy region in fig. 1 where P_{00}^{R} (total) exhibits structure.

4. Discussion and conclusions

There is more structure in fig. 1 than we anticipated; we had expected most of the structure seen in reduced dimensional quantum calculations to be washed out in the 3D results. However, such is not really the case. BCRLM [21] calculations for zero angular momentum show peaks in P_{00}^{R} (total), $P_{00}^{R}(2)$, $P_{00}^{R}(3)$, and $P_{00}^{R}(4)$ which are clearly analogous to the present peaks at 1.66, 2.06, 2.1 and 2.2 eV and most of which are nearly as wide as the present peaks. Collinear calculations [21] show peaks between 1.98 and 2.15 eV which are narrower and not so directly analogous. However, neither of the reduced dimensional calculations shows anything analogous to the dip in P_{00}^{R} (total) and $P_{00}^{R}(3)$ at 1.8 eV or the peaks in $P_{00}^{R}(2)$ at 1.72, 1.82 and 2.04 eV; the corresponding BCRLM and collinear results are smooth. Whether the 3D results for J > 0 (which must be included to calculate cross sections) will wash out some of the structure in fig. 1 remains to be seen. We intend to generate J > 0 information in future work.

We also plan a detailed analysis of the scattering



matrices, Argand diagrams, time delays, and adiabatic potential curves to elucidate the nature and source of the present structures, and that will be reported elsewhere [19]. At present, we simply mention a few possibilities.

The sharp peak in P_{00}^{R} (total) and $P_{00}^{R}(3)$ near 2.06 eV is very likely a closed channel resonance since it occurs just before the opening of the $v_f=4$ channel (2.092 eV). The small peak in P_{00}^{R} (total) and $P_{00}^{R}(2)$ between the threshold for reaction (1.645 eV) and the opening of the $v_f=3$ channel at 1.664 eV may also be due to a closed channel resonance.

The structure in fig. 1 between 1.7 and 1.9 eV seems connected with changes in the final rotational state distributions as shown in figs. 2a-2c. In fig. 2a at 1.78 eV, the $v_{\rm f}$ = 2 rotational distribution is broad and smeared out across all energetically allowed values of $j_{\rm f}$. However, in fig. 2b at 1.82 eV we see a very inverted rotational population in $v_f=2$ (i.e. a large increase in the probabilities for forming HF in high rotational states). By 1.86 eV (fig. 2c) the peak in $v_{\rm f}=2$ at large $j_{\rm f}$ is rapidly subsiding and a second peak is appearing at low j_{f} . At the same time, a more subthe change occurs in the $v_{\rm f}$ = 3 rotational distribution in figs. 2a–2c: the peak in the $v_f=3$ distribution shifts from $j_f = 1$ to $j_f = 2$ and $P_{00}^{R}(3)$ grows (see fig. 1) since the $i_f=0$ and 1 probabilities remain nearly constant as the $j_f \ge 2$ probabilities increase. Equally fascinating changes in rotational state distributions also occur in connection with the structures in fig. 1 at higher energies. These effects in the rotational distributions in $v_{\rm f} = 2$ and 3 bespeak a rather highly quantized rotational motion for this system. We do not yet know the underlying causes of this behavior but will probe it in future work [19].

Another feature of the F+H₂ quantum dynamics for J=0 on the T5A PES, apparent in fig. 1, is that $P_{00}^{R}(3)$ is greater than $P_{00}^{R}(2)$ at every energy above the v_{f} =3 threshold. However, the rate constants into v_{f} =2 are known experimentally [22] to be larger than those into v_{f} =3 for thermal rates corresponding to total energies peaked about 1.78 eV. We do not expect this dominance of $P_{00}^{R}(3)$ over $P_{00}^{R}(2)$ to persist for J>0. However, if it does persist, it will clearly indicate an error in some important region of the T5A PES. We note in passing that the calculations of Zhang and Miller [2] on the presumably less accurate M5 PES give $P_{00}^{R}(2) > P_{00}^{R}(3)$ for J=0 for energies near 1.78 eV.

In conclusion, we have presented benchmark accurate 3D full CC calculations of the reaction probabilities for the $F+H_2$ reaction for J=0 using the realistic T5A PES and have demonstrated their convergence. The significant structure in the reaction probabilities with energy and the rapid changes in rotational distributions suggest strong quantum resonance effects.

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