

Accurate three-dimensional quantum scattering calculations for $F + H_2 \rightarrow HF + H$ with total angular momentum $J = 1$

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Accurate 3D coupled channel calculations with total angular momentum $J = 1$ are presented for the reaction $F + H_2 \rightarrow HF + H$ for the T5a potential of Truhlar and coworkers. Reaction probabilities for relative scattering energies up to 0.71 eV are reported. The APH hyperspherical formulation is used, and the adiabatic basis functions are generated using the discrete variable representation (DVR). The $J = 1$ reaction probabilities into final vibrational channels show less structure than the $J = 0$ results reported elsewhere.

1. Introduction

The $F + H_2$ reaction is the focus of both experimental and theoretical activity. The molecular beam experiments of Lee and coworkers [1] have certainly motivated the theoretical efforts, as the observed differential cross section for scattering into the $v = 3$ vibrational product state clearly shows the evidence of quantum dynamical resonances.

On the theoretical side, many classical, and colinear and approximate 3D quantum calculations have been performed. In the interest of brevity, we review only 3D coupled channel (CC) calculations for this reaction, which is very challenging due to its high exoergicity. Calculations for total angular momentum $J = 0$, utilizing the M5 potential energy surface (PES) of Muckerman [2], have been reported by two groups [3,4]. However, the majority of CC calculations have utilized the T5a PES of Truhlar and coworkers [5], as it is believed to be more realistic than the M5 PES. For $J = 0$ on the T5a PES, hyperspherical calculations have been reported by Bačić and ourselves [6,7], and variational calculations have been reported by others [8–11]. (We note that some [3,10] of the above calculations are not fully converged.) Also variational $J = 0$ calculations for the

isotopic variants of H_2 should soon be forthcoming ($F + HD$ [12] and $F + D_2$ [13]).

In this Letter, we present converged 3D calculations for $J = 1$ using the T5a PES and the APH–DVR scattering method summarized below. Relative collision energies, E_{rel} , up to 0.71 eV are considered. Recently, Yu et al. [9] have reported variational $J = 1$ calculations for E_{rel} up to 0.19 eV and a $J = 2$ calculation for $E_{\text{rel}} = 0.08$ eV.

2. Theory and calculation

The computational methods have been described in detail previously. The reactive scattering is formulated using adiabatically adjusting principal axis hyperspherical (APH) coordinates [14]. The solutions to the total scattering wavefunction are expanded in a basis of sector adiabatic surface functions. These surface functions are bound state solutions of the surface Hamiltonian, which is a function of the two APH hyperangles θ and χ , and which depends parameterically on the APH hyper-radius ρ_ξ . The surface functions are calculated at many values of ρ_ξ , $\xi = 1, 2, \dots, n$, using the discrete variable representation (DVR) method [15]. Specific application of the DVR sequential diagonalization-truncation [16] procedure to the calculation of surface functions is described in ref. [7]. When

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the expression for the total scattering wave function is substituted into the full Schrödinger equation for a given J and total energy E (measured from the bottom of the asymptotic HF well), a set of N coupled channel (CC) equations is obtained, where N is the number of surface functions in the CC expansion. The log-derivative [17] method is used to propagate these exact CC equations from ρ_1 to ρ_n and the boundary conditions are applied as usual [14].

In this Letter, solutions for $J=1$ of even parity $p=0$ are considered. This situation was studied previously [18] for the the H+H₂ reaction, where it was shown that only the $A=1$ body-fixed component of J occurs in the CC expansion. In the terminology of ref. [18], the present surface functions are calculated as a CC basis, where the asymmetric top coupling term which is diagonal in $A=1$ is included with the surface Hamiltonian. In the propagation, symmetry decoupling is used, so that scattering out of even initial j_i rotor states of H₂ means that only surface functions which correlate with even j in the H₂ arrangement channel are needed. Also, $j_i=0$ is not allowed for $J=1$ and even parity, since $j_i \geq A=1$ is required. Thus, the lowest allowed even initial rotational state is $j_i=2$.

Next, we specify the finite basis representation (FBR) and input parameters needed for the DVR calculations. For θ , a FBR of (normalized) Legendre polynomials in $\cos 2\theta$, $\{\hat{P}_l(\cos 2\theta), l=0, 1, \dots, l_{\max}\}$, was used. The choice for the FBR in χ which corresponds to initial states of even j , even parity and $A=1$ is the set of symmetry-adapted [19] (normalized) functions $\{\pi^{-1/2} \sin(2m\chi), m=1, 2, \dots, m_{\max}\}$. Convergence studies similar to those conducted [7] for $J=0$ showed that $l_{\max}=50$ and $m_{\max}=110$ (the values used in the present production run), provided at least four figures of convergence for the 98th, 99th, and 100th surface function eigenvalues at $\rho_\xi=9.5 a_0$ ($1 a_0=1$ bohr unit). A linear interpolation similar to that used [7] for $J=0$ defined the ray eigenvector cutoff, E_{cut} on the interval $\rho_\xi=[2.2, 4.028] a_0$. For $\rho_\xi \geq 4.028 a_0$, $E_{\text{cut}}=4.0$ eV. The potential energy cutoff V_{\max} was set to $1.75 E_{\text{cut}}$ for all values of ρ_ξ .

The parameters used in the propagation of the CC equations are the same as those used for the converged $J=0$ calculations [7]. These parameters were: $N=150$; initial and final ρ_ξ of 2.2 and $9.405 a_0$, re-

spectively; ρ_ξ spacing of $\Delta\rho_\xi=0.01$; and the approximate number of log-derivative steps per de Broglie wavelength, $n_\lambda=20$. The asymptotic correlation of the adiabatic surface function bases is expressed in the following notation where (j_0, j_1, \dots, j_v) denotes the highest j state included within the v vibrational manifold. The correlations for $N=150$ are: for the H₂ channels (12, 8, 4); and for the HF channels (32, 29, 25, 22, 17, 11).

3. Results, discussion and conclusions

Distinguishable particle reaction probabilities $[P_{02}(v_f)]$ for $J=1, p=0$ are shown in fig. 1 and convergence studies are presented in tables 1 and 2. The reaction probability summed over final open rotational states is

$$P_{02}(v_f) = \sum_{j_f} P_{02}(v_f, j_f), \quad (1)$$

where $P_{02}(v_f, j_f)$ is the state-to-state reaction probability from the initial H₂ rovibrational state ($v_i=0, j_i=2$) into both HF arrangement channels of final rovibrational state (v_f, j_f). Although three figures are reported in tables 1 and 2 for comparative purposes, the probabilities are certain to about two significant figures. To convert the results to E_{rel} , the energy of

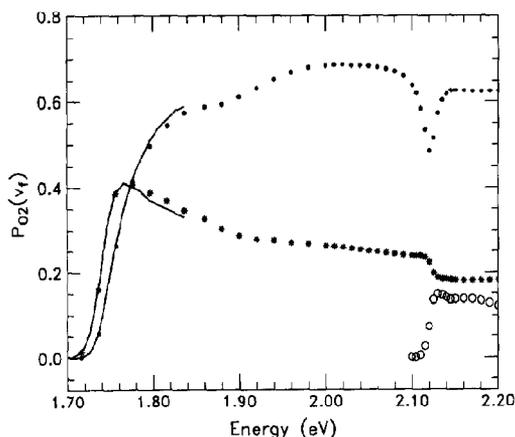


Fig. 1. F+H₂ reaction probabilities $P_{02}^R(v_f)$ for $J=1, p=0$ plotted versus total energy E . Legend: (*) $v_f=2$; (●) $v_f=3$; (○) $v_f=4$. The lower and upper lines are the results of Yu et al. [9] for $v_f=2$ and $v_f=3$, respectively. $E_{\text{rel}}=E-1.6894$ eV.

Table 1

A convergence study of $F+H_2$ reaction probabilities for $J=1$, even parity, and initial state ($v_i=0, j_i=2$). $E_{\text{rel}}=E-1.6894$ eV

Total energy E (eV)	Method	$N^a)$	$P_{02}(v_f)$		
			$v_f=1$	$v_f=2$	$v_f=3$
1.7167	APH ^{b)}	130	0.984(-3) ^{d)}	0.139(-1)	0.151(-2)
		140	0.991(-3)	0.140(-1)	0.149(-2)
		150	0.993(-3)	0.140(-1)	0.154(-2)
	VAR ^{c)}	130	0.92(-3)	0.14(-1)	0.15(-2)
		140	0.92(-3)	0.14(-1)	0.15(-2)
		150	0.92(-3)	0.14(-1)	0.15(-2)
1.7567	APH	130	0.237(-1)	0.388	0.263
		140	0.237(-1)	0.386	0.263
		150	0.236(-1)	0.385	0.263
	VAR	130	0.22(-1)	0.39	0.27
		140	0.22(-1)	0.39	0.27
		150	0.22(-1)	0.39	0.27
1.7967	APH	130	0.206(-1)	0.387	0.496
		140	0.207(-1)	0.388	0.497
		150	0.207(-1)	0.387	0.497
	VAR	130	0.17(-1)	0.37	0.51
		140	0.17(-1)	0.37	0.51
		150	0.17(-1)	0.37	0.51
1.8367	APH	130	0.168(-1)	0.346	0.574
		140	0.167(-1)	0.347	0.574
		150	0.168(-1)	0.346	0.574
	VAR	130	0.13(-1)	0.33	0.59
		140	0.13(-1)	0.33	0.59
		150	0.13(-1)	0.33	0.59

^{a)} N is the number of channels (surface functions). ^{b)} Present results. ^{c)} Variational results of Yu et al. [9].^{d)} $0.984(-3)=0.984 \times 10^{-3}$.

Table 2

 $F+H_2$ reaction probabilities for $J=1$, even parity, initial state ($v_i=0, j_i=2$), and total energy $E \geq 1.9$ eV. $E_{\text{rel}}=E-1.6894$ eV

Total energy E (eV)	$N^a)$	$P_{02}(v_f)$			
		$v_f=1$	$v_f=2$	$v_f=3$	$v_f=4$
1.9	140	0.160(-1) ^{b)}	0.288	0.609	0.0
	150	0.160(-1)	0.288	0.610	0.0
2.0	140	0.114(-1)	0.262	0.686	0.0
	150	0.114(-1)	0.264	0.685	0.0
2.1	140	0.189(-1)	0.239	0.640	0.177(-3)
	150	0.191(-1)	0.238	0.639	0.261(-3)
2.2	140	0.867(-2)	0.179	0.625	0.124
	150	0.887(-2)	0.182	0.625	0.122
2.3	140	0.900(-2)	0.127	0.531	0.228
	150	0.885(-2)	0.128	0.533	0.228
2.4	140	0.566(-2)	0.101	0.498	0.255
	150	0.608(-2)	0.101	0.499	0.254

^{a)} N is the number of channels (surface functions). ^{b)} $0.160(-1)=0.160 \times 10^{-1}$.

the initial state, given in tables 1 and 2, must be subtracted from the total energy E .

The probabilities in table 1 for $N=150$ are con-

verged to two figures or better with respect to N channels (surface functions). The results of Yu et al. [9], which are claimed to be converged to 1% for the

larger probabilities ($P_{02}(2)$ and $P_{02}(3)$), are also presented in table 1 and plotted in fig. 1. For the larger probabilities in table 1, the present results and those of Yu et al. [9] agree to better than 5%. From this agreement and because two completely different methods were used (the present APH-DVR versus their variational), we conclude that both calculations are correct on the total energy interval [1.7167, 1.8367] eV. Where they differ, we feel that the present results are probably more accurate than those of Yu et al. [9] as the present results are converged with respect to N to better than 1%. However, this conclusion is not absolutely certain as convergence was not explicitly checked with respect to all the other propagation parameters listed above, but the same values for these parameters yielded fully converged results for $J=0$ [7]. Also, convergence of the present surface functions with respect to the DVR parameters is similar to that studied in detail for the converged $J=0$ calculations [7].

The reaction probabilities for higher energies, which are presented in table 2, also appear to be converged to two figures with respect to N , except for the threshold value of $P_{02}(4)$ at 2.1 eV, which is converged to one figure.

Comparing the present results for $J=1$ with those for $J=0$ (fig. 6 of ref. [7]), we note some differences and trends. The present $J=1$ probabilities show much less structure over the whole energy range. At threshold, the $P_{02}(v_f=2)$ is greater than $P_{02}(v_f=3)$, as noted by Yu et al. [9], but for $E \geq 1.8$ eV, the inequality is reversed. The known thermal rates [20] are greater for $v_f=2$ than for $v_f=3$. The 300 K Boltzmann distribution that would be used to calculate contributions to the thermal rate from $(v_i=0, j_i=2)$ peaks at 1.72 eV and has its half maxima at 1.70 and 1.76 eV. Thus, the $J=1$ probabilities are somewhat more favorable in this respect than those for $J=0$ where $P_{02}(v_f=3)$ was greater than $P_{02}(v_f=2)$ for all E . The question of whether the T5a PES can provide thermal rates which agree with experiment will only be answered with certainty when converged integral cross sections are constructed (which will probably need J values of 30 or more). Work in this direction is in progress utilizing analytic primitive basis functions which increase the speed of the surface function calculations.

A closed channel resonance near 2.1 eV in fig. 1,

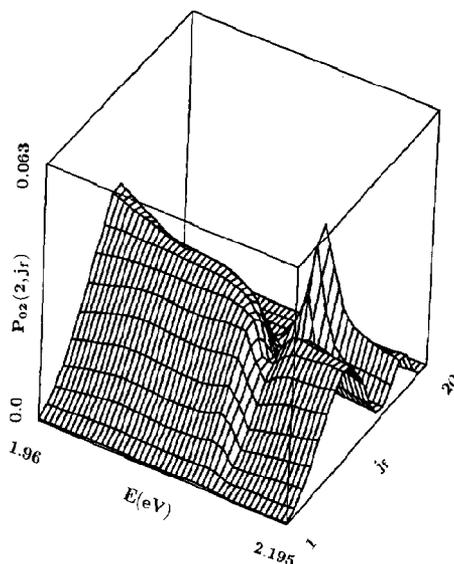


Fig. 2. F+H₂ state-to-state reaction probabilities $P_{02}^{P_3}(v_f, j_f)$ for $J=1, p=0$ and $v_i=2$ plotted versus total energy E and final rotational state j_f .

due to the opening of the $v=4$ channel, was also observed for the $J=0$ calculations [7]. The present calculations were performed at 0.005 eV intervals in this resonance region; the center of the sharp dip in $P_{02}(v_f=3)$ is at 2.120 eV. This resonance also appears clearly in fig. 2, where state-to-state reaction probabilities $P_{02}(v_f, j_f)$ for $v_f=2$ are shown as a function of total energy and of final rotational state j_f . The most probable j_f value, defined as $\max(j_f)$, hovers about a value of 8 to 10 at all energies *except* near the resonance at 2.12 eV. At the resonance, $\max(j_f)$ shifts abruptly to 16 and then back down to 8 again. Behavior similar to this was observed in the plots of $P_{00}(2, j_f)$ for $J=0$ [7], although only a shoulder was seen at large j_f at the resonance energy in contrast to the sharp peak in fig. 2.

In conclusion, we have presented accurate 3D CC calculations with nonzero $J(=1)$ for the F+H₂ reaction. The present calculations for $E_{\text{tot}}=[1.7167, 1.8367]$ eV are in good agreement with the variational results of Yu et al. [9], and the present results for $E_{\text{tot}}=[1.86, 2.40]$ eV provide, we believe, a benchmark.

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