A quasiclassical trajectory study of the \( \text{F}+\text{HH} \leftrightarrow \text{FH}+\text{H} \) reaction

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A detailed forward and reverse quasiclassical trajectory computation for the FHH reaction is presented. An adiabatic analysis of the results shows that to a large extent the differences between HF(\( \nu = 3 \)) and HF(\( \nu = 2 \)) product distributions are due to the existence of an exit channel adiabatic barrier for the \( \nu = 3 \) state. A sideways peak in the angular distribution for HF(\( \nu = 2 \)) is found in the reverse quasiclassical computation. Total cross sections computed from reverse quasiclassical trajectories are in good agreement with the quantal \( L_n \) reactive infinite order sudden approximation. We conclude that many of the discrepancies between forward quasiclassical results and quantal computations are not due to quantal resonances but rather to the large boxing of vibrational states.

I. INTRODUCTION

The FHH system is currently one of the most intriguing “simple” chemical exchange processes. The recent detailed molecular beam experiments\(^1\) have shown that the angular distribution of products is a sensitive function of the product state. For the ground state reaction of fluorine atoms it was observed that the angular distribution of the product HF(\( \nu = 2 \)) molecule changes, as reagents translational energy is increased, from backward peaked to sideways peaked while the HF(\( \nu = 3 \)) angular distribution remains at both energies backward peaked.

Theoretical analysis of this system is extensive. Prior to the molecular beam experiments, Redmon and Wyatt\(^6\) using the \( j_k \) conserving decoupling method\(^7\) performed a 3D quantal computation. Their results, based on the Muckerman \( V \) potential energy surface,\(^4\) emphasized the dependence of the various vibrational state to state cross sections on energy and total angular momentum \( J \). They found for the \( (\omega_f = 0 - \omega_f = 2, J) \) transition that the maximum of this distribution shifted to higher \( J \) values as energy was increased. However for the \( (\omega_f = 0 - \omega_f = 3, J) \) distribution the maximum remained at \( J = 0 \) at all energies. More recently Wyatt et al.\(^5\) have shown that the ridge in the HF(\( \nu = 2 \)) distribution could be interpreted in terms of a quantal resonance. Analysis of the phase shifts showed relatively large time delays in the vicinity of “resonance ridge.” Using an optical model Wyatt has shown\(^8\) that the shift in the HF(\( \nu = 2 \)) angular distribution may be correlated with a resonance ridge. It was thus proposed that the experimental observation of the sideways shift was the first experimental verification of quantal Feshbach type resonances in reactive scattering.

A different quantal analysis based on the reactive infinite order sudden approximation (RIOSA) was given by Baer, Jellinek, and Kouri.\(^9\) This treatment was the first internally consistent theory which gave 3D angular distributions for the FHH system, in good accord with experiment.\(^7\) At low translational energies (0.043, 0.073, 0.089 eV) it was found that all three product angular distributions \( (\nu_f = 1, 2, 3) \) were backwards peaked in agreement with the experiment at 0.087 eV. For higher translational energies (0.156, 0.233 eV) the \( \nu_f = 3 \) distribution remained backward peaked while the \( \nu_f = 2 \) (0.156 eV) and the \( \nu_f = 1 \) (0.233 eV) distributions became sideways peaked. A detailed analysis of the orbital angular momentum and angular dependence of the RIOAS matrix elements and probabilities\(^1\) showed that the sideways shift could be due to quantum Feshbach resonances. Phase shift analysis also supported this picture. However these authors noted that it is possible that other dynamical effects such as exit channel constraints can give rise to a similar effect in the angular distributions.

Most recently, Redmon and Wyatt\(^8\) also obtained converged angular distributions. Again, they found a definite (strong) sideways peak in the HF(\( \nu = 2 \)) distribution which was absent at HF(\( \nu = 3 \)).

Emmons and Suck\(^5\) have suggested, based on distorted wave Born (DWBA) computations, that the angular shift may be due to an increase in the number of participating partial waves.

A very recent 3D quasiclassical trajectory computation of Blais and Truhlar\(^9\) seems to corroborate the resonance mechanism. In this work quasiclassical trajectories were initiated from the ground vibrational and rotational state of hydrogen. The products were boxed according to the usual boxing scheme. Here there was no qualitative difference between the HF(\( \nu = 2 \)) and HF(\( \nu = 3 \)) angular distributions. Therefore this work implies that the effect is a quantal one. Of course, quantal Feshbach resonances will not be seen in quasiclassical computations.
The computations of Blais and Truhlar are actually of much more general concern than the bare question of whether there is or is not a quantal resonance. Their computations show serious qualitative discrepancies between all available quantal theories and the quasi-classical computations. If there are qualitative differences in the angular distribution then the total cross sections are possibly also unreliable. In fact, the quasi-classical total cross section is over a factor of 2 larger than that calculated by the $I_{el}$ RIOS\textsuperscript{5} and the $I_{el}$ conserving\textsuperscript{6} approximations (although it should be mentioned that the $I_{el}$ RIOSA\textsuperscript{5} yields total reactive cross sections reasonably close to the quasi-classical forward results). Furthermore, at low energies, the quasi-classical computations of Connor et al.\textsuperscript{11} (which are in good agreement with the Blais and Truhlar work) show that the classical ratio of HF ($\nu = 3$) to HF ($\nu = 2$) products is much larger than all quantal predictions, so if one summarizes, there is a qualitative discrepancy between quasi-classical trajectory computations and quantal computations for total cross sections, product vibrational distributions, and angular distributions. If so, is the quasi-classical approach at all reliable?

For the FH system it is well known that for both the collinear\textsuperscript{12} and 3D cases,\textsuperscript{13} reverse quasiclassical trajectories give results that are qualitatively different from the forward computations. Most notably, the HF ($\nu = 3$) dynamical threshold is well accounted for by the reverse computation but not by the forward. Pollak has shown\textsuperscript{14} that the quantal dynamical threshold is due to an adiabatic exit channel barrier on the adiabatic $\nu = 3$ potential energy surface. Since motion from products to the barrier is also classically vibrationally adiabatic, one will feel the barrier if one initiates trajectories with HF having exactly 3.5 h vibrational action. However if one starts on the HH side and puts all reactive trajectories that have 3-4 h vibrational action into HF ($\nu = 3$) one will have smeared the barrier. The adiabatic threshold for 3 h action is much lower than that for 3.5 h action.

The adiabatic analysis has shown that there is a qualitative difference between the $\nu = 2$ and $\nu = 3$ vibrationally adiabatic potential energy surfaces. For $\nu = 2$ there is only a single barrier located in the entrance channel. For $\nu = 3$ an adiabatic barrier exists in the exit and entrance channels. Is it possible that the exit channel barrier for $\nu = 3$ is responsible for the differences between the quantal and forward quasiclassical computations?

In this paper we show that the exit channel barrier plays an important role. Reverse quasiclassical trajectories show qualitative differences in the angular distributions of HF ($\nu = 2$) and HF ($\nu = 3$). In addition, using microscopic reversibility\textsuperscript{15} we find total cross sections which are in much better agreement with the quantal cross sections.

This paper is organized as follows: In Sec. II we analyze in detail the $\nu = 3$ adiabatic barrier in the exit channel. We use a recently formulated adiabatic RIOS transition state theory\textsuperscript{16} to predict total cross sections from HF ($\nu = 3$). In Sec. III we provide detailed reverse quasiclassical trajectory results. We then use microscopic reversibility to assess the forward (F + H$_2$) cross sections obtainable from the reverse results. In Sec. IV we discuss the implications of our analysis on quasi-classical trajectory computations in general paying special attention to Miller's classical limit trajectory method.\textsuperscript{17} We also discuss the implications of our results on the question of the existence of a resonance effect in the FH system.

II. THE HF ($\nu = 3$) ADIABATIC BARRIER

As has been described previously we find adiabatic barriers with the aid of periodic orbit dividing surfaces (PODs).\textsuperscript{14} Collinearly an adiabatic barrier (or well) on the $\nu$th adiabatic potential energy surface corresponds to a pods whose action over one period of motion is $(\nu + 1/2) h$. In Ref. 14 it has been shown that the FH system on the Muckerman V LéEPS potential surface has a noticeable (0.08 eV) barrier in the exit channel for the $\nu = 3$ collinear adiabatic surface. Here we apply a recently proposed adiabatic infinite order sudden transition state theory\textsuperscript{16} to estimate the effects of this barrier in a 3D collision.

We let $\gamma_{R}$ denote the angle between $r_{HF}$—the HF internuclear distance, and $r_{HF-H}$—the H atom to HF center-of-mass distance. The dynamics for a fixed value of $\gamma_{R}$ are equivalent to those of a two degree of freedom system. Thus, for each $\gamma_{R}$ one can look for the pods corresponding to the $\nu = 3$ adiabatic barrier. We denote the $\gamma_{R}$ dependent energy of the barrier as $E_{b}(\gamma_{R})$. The minimum energy path of the Muckerman V potential energy surface is collinear so that we expect $E_{b}(\gamma_{R})$ to be minimal at the collinear configuration ($\gamma_{R} = 0$).

The $\nu = 3$ barrier in the exit channel is dynamic in nature. The saddle point of the surface is of course in the entrance (HH) channel. As has been shown in other cases,\textsuperscript{18} increasing the angle while keeping the action of the orbit fixed is in a sense equivalent to keeping the angle constant and decreasing the energy. Collinearly, the generic behavior is that at high energies one has three pods.\textsuperscript{19} As energy is decreased, two pods—those that are not in the saddle point region, coalesce and disappear. Finally, below the saddle point energy the remaining pods disappear. Thus for the $\nu = 3$ barrier we expect to find a maximal angle at which the two pods corresponding to the adiabatic barrier and adiabatic well in the exit channel (HF) side coalesce and disappear. In other words the $\nu = 3$ exit channel barrier is well defined only for a restricted set of angles. Numerically, we found that the maximal angle is $20^\circ \pm 0.5^\circ$.

The RIOS Hamiltonian in the exit channel $\nu$ (for convenience we drop the $\nu$ label) has the form\textsuperscript{20}

$$H = -\frac{h^2}{2M} \frac{d^2}{dr^2} - \frac{\mu^2}{2M} \frac{d^2}{dr^2} + \frac{\mu^2 (\tilde{I} + 1)}{2MR^2} + \frac{\mu^2 (\tilde{f} + 1)}{2mv^2} + \nu (\nu, R, \gamma).$$

(1)

Here $m$ is the HF reduced mass, $M$ is the atom–diatom reduced mass, and $\tilde{I}$ and $\tilde{f}$ are the orbital and rotational quantum numbers which are treated as parameters in the RIOS formalism. Finding the adiabatic barrier implies
TABLE I. Parameters of the HF(ν = 3)
adibatic barrier.

<table>
<thead>
<tr>
<th>cos γ</th>
<th>E₁(γ) (^a)</th>
<th>B₁(γ) (^b)</th>
<th>B₂(γ) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.3713</td>
<td>17.82</td>
<td>2.94</td>
</tr>
<tr>
<td>0.99</td>
<td>0.3765</td>
<td>17.71</td>
<td>3.05</td>
</tr>
<tr>
<td>0.98</td>
<td>0.3826</td>
<td>17.58</td>
<td>3.18</td>
</tr>
<tr>
<td>0.97</td>
<td>0.3897</td>
<td>17.41</td>
<td>3.32</td>
</tr>
<tr>
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<td>0.3962</td>
<td>17.18</td>
<td>3.48</td>
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<td>0.95</td>
<td>0.4085</td>
<td>16.93</td>
<td>3.67</td>
</tr>
<tr>
<td>0.94</td>
<td>0.4213</td>
<td>16.51</td>
<td>3.91</td>
</tr>
</tbody>
</table>

\(^a\)Energies in eV relative to the bottom of the asymptotic HH well. The asymptotic HF(ν = 3) level is at 0.238 eV.
\(^b\)Rotational constants are given in cm\(^{-1}\).

finding for each \(\gamma_j, I, j\) a pods with 3.5 h action. One can simplify by noting that the angular momentum terms should in any case be small if the RIOS is to be useful. Thus we treat these terms as a perturbation. One can then show\(^16,18\) that within the framework of first order classical perturbation theory the adiabatic barrier levels are

\[ E_n, I, j(\gamma) = E_n(\gamma) + B_1(\gamma)I(I + 1) \pm A_1(\gamma)J(J + 1). \]  

(2)

Here \(E_n(\gamma)\) is the angle dependent barrier of the \(n\)th state for \(I = 0, j = 0 \) and \(B_1(\gamma)\) and \(A_1(\gamma)\) are orbital and rotational constants respectively:

\[ B_1(\gamma) = \frac{1}{T_0(\gamma)} \int \frac{d\theta}{2Mr^2(\theta)} h^2, \]

(3)

\[ A_1(\gamma) = \frac{1}{T_0(\gamma)} \int \frac{d\theta}{2Mr^2(\theta)} h^2. \]

(4)

The constants are found by averaging the instantaneous moment of inertia over the period \(T_0(\gamma)\) of the pods corresponding to the adiabatic barrier with \(I, j = 0\).

Given the adiabatic levels it is easy to give a transition state theory like evaluation of the cross section. We assume that reaction occurs with unit probability provided that the reagents (HF) energy \(E\) is greater than the barrier height:

\[ P_{n, I, j}(\gamma, E_T) = \theta [E - E_{n, I, j}(\gamma)]. \]

(5)

Here \(P_{n, I, j}(\gamma, E_T)\) is the total reaction probability to all possible final product states for reactants with translational energy \(E_T\) and in the \(n\)th vibrational, \(I\)th rotational, and \(j\)th orbital angular momentum state. \(\theta\) is the unit step function and \(E\) is the total energy

\[ E = E_T + E_{n, I, j}, \]

(6)

where \(E_{n, I, j}\) is the vibrational energy of reactants.

Using the TST assumption we have shown\(^18\) that the angle dependent total cross section is given by a simple line of centers expression

\[ \sigma_{n, I, j}(\gamma) = \frac{\pi h^2}{2MB_n(\gamma)} \left[ 1 - \Delta E_{n, I, j}(\gamma)/E_T \right] \theta [E_T - \Delta E_{n, I, j}(\gamma)], \]

(7)

where

\[ \Delta E_{n, I, j}(\gamma) = E_n(\gamma) + A_1(\gamma)J(J + 1) - E_{n, I, j}. \]

(8)

The total reactive cross section is obtained by averaging the angle

\[ \sigma_{n, j}(E_T) = \frac{1}{2} \int_0^{\pi} \sigma_{n, I, j}(\gamma, E_T) \sin \gamma d\gamma. \]

(9)

In Table I we provide the ν = 3 adiabatic barrier \(\gamma\) dependent constants. In Fig. 1 we plot the angle dependent total cross section as a function of \(\gamma\) and \(J\) for two total energies. To obtain the total cross section [cf. Eq. (9)] one must integrate over all possible \(\gamma\) values. At \(E = 0.423\) eV this is straightforward. However at \(E = 0.5\) eV a problem arises. Strictly speaking, as mentioned earlier the adiabatic barrier does not exist beyond \(\cos \gamma < 0.94\). However from the shape of the \(\gamma\) dependence of the cross section at \(0.423\) eV it seems that a linear extrapolation to larger angles can only give an overestimate of the cross section. This linear extrapolation is shown as the dashed lines in Fig. 1.

The total cross sections are shown as a function of \(J\) at the two energies in Fig. 2. Also shown are the re-
results of the quasiclassical trajectory computations. We find that the adiabatic RIOS overestimates the quasiclassical cross section by a factor of 2–3. This is reasonable if one remembers that the adiabatic theory is in a sense an upper bound.† It gives the probability of entering the strong coupling region of the potential energy surface. Entering the strong coupling region does not ensure a reactive trajectory, the trajectory can still be back reflected. In fact the collinear reverse reaction probability from H\(\text{F}(v = 3)\) at this energy is 0.4.‡ Note also that the adiabatic theory estimates correctly the maximal \(J\) for which reaction is allowed.

Finally we note that Eqs. (2) and (5) enable us to evaluate \(I_{\text{maj}}\) for each value of \(J\). Since the minimum of \(E_{\text{nuc}}(\gamma)\) is in our case at \(\gamma = 0\) it is easy to see that

\[
I(J + 1) \leq \frac{[E - E_{\text{nuc}}(0) - \mu_{\text{H}}(0)J(J + 1)]}{B_{\text{nuc}}(0)}. \tag{10}
\]

The solid line in Fig. 3 shows \(I_{\text{maj}}\) as a function of \(J\) (at \(E = 0.5\) eV) as calculated from Eq. (10). The solid circles are upper bounds to \(I_{\text{maj}}\) found from the reverse quasiclassical computations described in the next section. They are obtained from the maximal impact parameter used in the trajectory computations [for \(J = 0, 2, 4, 7, b_{\text{max}} = 4, 4, 4, 2\) (bohr) respectively]. Evidently, the adiabatic barrier serves to restrict the range of \(I\) values that contribute to the reaction. Note also that this plot implies that the maximal total angular momentum at which reaction into the \(v = 3\) channel is allowed is 20. This is in quantitative agreement with the \(J_{\text{cons}}\) conserving computations of Redmon and Wyatt. ⁴ It falls however below the value of \(I = 28\) which was found by Blais and Truhlar¹⁰ in their forward trajectory computations.

III. QUASICLASSICAL TRAJECTORIES FOR FHH

A. The forward direction—F + HH → FH + F

Extensive quasiclassical computations for the forward direction are available.¹⁶,¹¹ The main purpose of this subsection is to show that in general our results are in good agreement with those previously published. In addition, we have computed some rotational cross sections which will be put to good use in the next section when we deal with the question of microscopic reversibility.

The quasiclassical trajectory method is well known and needs no further explanation. All results are for the Muckerman V LIPS potential energy surface. All computations are at \(E = 0.5\) eV relative to the bottom of the asymptotic HH well. This energy is chosen since it is a good one for comparison. Results from RIOS,⁶,⁷ \(J_{\text{cons}}\) conserving,⁸,⁹ and quasiclassical computations¹⁰ are available at this energy. This energy is slightly larger than the (higher) experimental energy.¹ The hydrogen molecule was initiated in the ground vibrational and rotational state.

5887 trajectories were run in the forward direction of which approximately one third are reactive. Using the standard boxing method for products [all trajectories with final vibrational action in the interval \(\{\hbar n, (n + 1)\hbar\}\) belong to the \(n\)th vibrational state, all trajectories with \(\{\hbar j, (j + 1)\hbar\}\) rotational action belong to the \(j\)th rotational state] we find the vibrationally resolved angular distributions shown in the top half of Fig. 4. The \(V_f = 2\) and \(V_f = 3\) distributions are practically identical to those of Blais and Truhlar,¹⁰ however \(V_f = 1\) is different. Whereas they found that the \(V_f = 1\) distribution is backwards peaked, we find a sideways shift of \(40°\). Note

![Fig. 4. Angular distributions of the forward reaction. Top panel, quasiclassical computation using standard boxing technique. Lower panel, fit RIOS results adapted from Ref. 6. Note that the same scale is used for all distributions. For the \(V_f = 3\) quasiclassical distribution we found one trajectory at 0.16°. This single trajectory (not shown in the figure) would give a differential cross section at the 0°–1° box of 3 (bohr)². Since statistics here are not good (only four trajectories in this box) we are not sure that this single trajectory is meaningful and so do not show it in the figure.](image-url)
that there are differences between the two computations. We used a larger number of trajectories. Blais and Truhlar use a Legendre moment method for the angular distributions while we boxed trajectories into $10^7$ intervals and then performed a running average (using three boxes each time). Note also that Blais and Truhlar did find a qualitative difference in the dependence of the reaction probability on initial orbital angular momentum $l_{in}$ between $v_f=1$ and $v_f=2,3$. For $v_f=1$ they find a maximum at $l_{in}=12,13$ while for $v_f=2,3$ the maximum is always at $l_{in}=0$. As shall be shown later on, the sideways shift in the $v_f=1$ distribution is not simply noise. We conclude that possibly for $v_f=1$ the Blais–Truhlar computation has not converged.

In the bottom half of Fig. 4 we show the vibrationally resolved angular distributions computed previously via the $l_{in}$ RIOS approximation. As noted by Blais and Truhlar there is a qualitative difference between the quantum and forward quasiclassical results.

The integral total and vibrational state to state cross sections as well as the various branching ratios are given in Table II. The results are compared with those obtained by other groups. We note that all our cross sections are in good agreement with those obtained by quasiclassical computations of other groups. We again note that the forward quasiclassical cross sections are twice as large as the quantum $l_{in}$ RIOSA and $j_f$ conserving results. We also note that the $\sigma(v=3)/\sigma(v=2)$ branching ratio predicted by the quasiclassical and $j_f$ conserving computations is twice as large as that predicted by the $l_{in}$ labeled RIOS.

Finally, in Fig. 5 we plot the vibrationally resolved product rotational cross sections. It is interesting to note that the most probable rotational state within a vibrational manifold increases noticeably as the vibrational energy decreases. In fact as predicted by Levine and Bernstein, the fractional energy of the most probable rotational state $f_R=E_R/E$ increases linearly as a function of $(1-f_R)$. This is easily rationalized in terms of the transfer of momentum constraint. If momentum is to be conserved then $f_R+f_e=\text{const}=1-f_T$. The importance of the transfer of momentum constraint—as shall be shown shortly—cannot be overstressed for this reaction.

### B. The reverse direction H + HF → HH + F

The only published reverse quasiclassical 3D computations that are known to us are those of Leasure and Bowman. These authors show that for HF $(v = 3)$ there is also in 3D a dynamic threshold which is in good quan-

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**TABLE II. Cross sections of the F + HH reaction.**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$v' = 0$</th>
<th>$v' = 1$</th>
<th>$v' = 2$</th>
<th>$v' = 3$</th>
<th>All $v'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present forward QCT calculations</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma(v')/\sigma(v' = 2)$</td>
<td>(0.0)$^a$</td>
<td>0.08</td>
<td>1.00</td>
<td>0.53</td>
<td>2.23$^c$</td>
</tr>
<tr>
<td>$\sigma(v')/\sigma(v' = 2)$</td>
<td>(0.0)$^a$</td>
<td>0.15</td>
<td>1.00</td>
<td>0.59</td>
<td>2.77</td>
</tr>
</tbody>
</table>

**QCT calculations of Blais and Truhlar (Ref. 10)**

| $\sigma(v')/\sigma(v' = 2)$ | 0.00 | 0.58 | 2.63 | 1.56 | 2.24 |
| $\sigma(v')/\sigma(v' = 2)$ | 0.00 | 0.22 | 1.00 | 0.49 | 2.28 |

**Classical RIOSA calculations of Jellinek and Baer (Ref. 29)**

| $\sigma(v')/\sigma(v' = 2)$ | (0.0)$^a$ | 0.24 | 1.54 | 0.45 | 2.24 |
| $\sigma(v')/\sigma(v' = 2)$ | 0.03 | 0.16 | 1.00 | 0.29 | 2.18 |

**$l_{in}$ labeled RIOSA calculation of Jellinek et al. (Ref. 6)**

| $\sigma(v')/\sigma(v' = 2)$ | (0.0)$^a$ | 0.28 | 1.84 | 0.50 | 1.78 |
| $\sigma(v')/\sigma(v' = 2)$ | 0.09 | 0.30 | 1.00 | 0.71 | 1.00 |

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$^a$All results are at $E = 0.5$ eV.

$^b$This is the total cross section for the reaction of HH in the ground vibrational state to the HF $(v')$ state summed over final rotational states within the $v'$ manifold.

$^c$All results are at $E = 0.5$ eV.

$^d$For explanations see Sec. III C.

$^e$These cross sections have not been computed but estimated using the $l_{in}$ results.

$^f$The total cross section is a sum of the estimated $v' = 0$ and $v' = 1$ cross sections and the "exact" computed $v'=2$ and $v'=3$ backwards cross sections.
TABLE III. State to state quasiclassical cross section for the reverse reaction \( H + HF(v_f,j_f) \rightarrow HH(v_i=0,j_i)+F \).^a

<table>
<thead>
<tr>
<th>( v_f )</th>
<th>( j_f )</th>
<th>( N^b )</th>
<th>( j_i=0 )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Total^c</th>
</tr>
</thead>
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<tr>
<td>2</td>
<td>0</td>
<td>11859</td>
<td>0.004</td>
<td>0.037</td>
<td>0.075</td>
<td>0.106</td>
<td>0.047</td>
<td>0.002</td>
<td>0.000</td>
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</tr>
<tr>
<td>4</td>
<td>0.013</td>
<td>0.055</td>
<td>0.094</td>
<td>0.071</td>
<td>0.052</td>
<td>0.003</td>
<td>0.000</td>
<td>0.287</td>
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<tr>
<td>7</td>
<td>0.013</td>
<td>0.085</td>
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<td>0.063</td>
<td>0.036</td>
<td>0.014</td>
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<tr>
<td>10</td>
<td>0.019</td>
<td>0.087</td>
<td>0.100</td>
<td>0.089</td>
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<td>0.020</td>
<td>0.036</td>
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<tr>
<td>12</td>
<td>0.021</td>
<td>0.062</td>
<td>0.079</td>
<td>0.079</td>
<td>0.058</td>
<td>0.033</td>
<td>0.033</td>
<td>0.366</td>
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<td>0.062</td>
<td>0.103</td>
<td>0.078</td>
<td>0.079</td>
<td>0.036</td>
<td>0.000</td>
<td>0.371</td>
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<td></td>
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<td>0.060</td>
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<td>0.049</td>
<td>0.418</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11884</td>
<td>0.065</td>
<td>0.164</td>
<td>0.090</td>
<td>0.029</td>
<td>0.347</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6122</td>
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<td>0.183</td>
<td>0.091</td>
<td>0.007</td>
<td>0.303</td>
<td></td>
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<td>7</td>
<td>4755</td>
<td>0.004</td>
<td>0.009</td>
<td>0.009</td>
<td>0.000</td>
<td>0.022</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a All cross sections are in \((\text{bohr})^2\). The total energy is 0.5 eV.
^b Total number of trajectories run with this initial condition.
^c The total cross section \( \sigma(v_f,j_f \rightarrow 0, j_i) \).

The table shows the state to state quasiclassical cross sections for the reverse reaction \( H + HF(v_f,j_f) \rightarrow HH(v_i=0,j_i)+F \). The total energy is 0.5 eV, and the total number of trajectories run with this initial condition. The total cross section for each set of initial conditions is also provided.

The second point involves the dependence of the total angular distribution on the total angular momentum \( J \). This is important because the HH phase space available is of course identical for both vibrational channels, the number of \( j \) states populated from the HF \((v=3)\) state is much smaller than the number populated from the HF \((v=2)\) state. This is indicative of a possible angular momentum restriction for the HF \((v=3)\) channel. We will elaborate further on this point in the next section.

Detailed state to state cross sections \( \sigma(v_f,j_f \rightarrow v_i=0,j_i) \) for the reverse reaction as well as numerical details of the computation are provided in Table III. Two important features of the distributions should be stressed. Although the HH phase space available is of course identical for both vibrational channels, the number of \( j \) states populated from the HF \((v=3)\) state is much smaller than the number populated from the HF \((v=2)\) state. This is indicative of a possible angular momentum restriction for the HF \((v=3)\) channel. We will elaborate further on this point in the next section.

FIG. 6. Angular distributions from reverse quasiclassical trajectories. Note that the scale used for all distributions is identical.
TABLE IV. Cross section for F + HH through microscopically reversing H + HF trajectories.

<table>
<thead>
<tr>
<th>$v_f$</th>
<th>$j_f = 0$</th>
<th>2$^a$</th>
<th>4</th>
<th>7</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>Total$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.013</td>
<td>0.321</td>
<td>0.462</td>
<td>0.685</td>
<td>0.590</td>
<td>0.240</td>
<td>5.916</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.057</td>
<td>0.285</td>
<td>0.147</td>
<td>0.018</td>
<td></td>
<td></td>
<td>1.058</td>
<td></td>
</tr>
</tbody>
</table>

$^a$All cross sections are in (bohr)$^2$. The energy is 0.5 eV.
$^b$Only $v_f = 3, j_f = 2$ trajectories were run.
$^c$The total cross section $\sigma(0,0 \rightarrow v_f, j_f)$ obtained by linear interpolation for missing $j_f$ values.

cross section on $j_f$ within a given vibrational manifold. For $v_f = 2$ the maximal cross section is for $j_f = 10, 12$. For these $j_f$'s the total internal energy (measured relative to the bottom of the HH well) of HF($v = 2, j_f = 10, 12$) is 0.13 and 0.25 eV, respectively. The energy of HH($v = 0$) is 0.27 eV. Thus the maximum of the distribution is another indication of the tendency of the FHH system to conserve translational energy. The magnitude of the maximal cross section for $v_f = 3$ further strengthens this point. HF($v = 3$) is at an energy of 0.29 eV. It is almost in resonance with HH($v = 0$).

The transfer of momentum is easy and so the maximal cross section is much larger than that obtained for $v_f = 2$. Of course the total cross section into $v_f = 3$ will be smaller because of statistics—the number of open $j$ states at $v_f = 2$ is much larger.

Finally we note that in the reverse results, the final rotational distribution ($j_f$) is only weakly dependent on the initial rotational state ($j_f$). For both $v_f = 2$ and $v_f = 3$, changing the initial rotational state just causes a broadening of the final rotational distribution but does not noticeably affect the location of the maximum.

C. Microscopic reversibility

In the previous section we have seen that there is a dramatic difference between the forward and reverse angular distributions of the FHH system. However to compare the reverse cross sections with quantal results one must reverse the quantal results via detailed balance. Unfortunately, to date, the complete vibrotational quantal cross sections are not available. Therefore we chose to use the detailed balance expression to reverse the classical results.

Quantally, microscopic reversibility implies$^{15,28} M_r E^r_f(2j_f + 1) \sigma(v_f, j_f \rightarrow v_i, j_i) = M_r E^r_f(2j_f + 1) \sigma(v_i, j_i \rightarrow v_f, j_f).

(11)

Here, $M_r$, $E^r_f$ ($M_r, E^f_f$) are the atom–diatom reduced mass and translational energy, respectively, in the final (initial) channel. Quantally, all computations have been made for HH in the ground rovibrational state. The quantity we must compute therefore is $\sigma(0,0 \rightarrow v_f, j_f)$. These cross sections as obtained from Eq. (11) and Table III are given in Table IV and plotted in Fig. 5. Since the reverse computation was made for only six initial $j$ values it is necessary to interpolate (linearly) between them to obtain the total cross section given in the table. Note also that for the forward direction there are two identical reaction channels. The forward cross sections as given in Table II are for the sum of the two channels. Thus the bare results from the reverse direction are multiplied by a factor of 2.

The total cross sections for the forward reaction appear in Table II under the heading "present reverse QCT computations." The $\sigma(v_f = 0,1)$ cross sections are too expensive to compute, the reaction probability from these states is too low. However, by the same token, these cross sections are relatively negligible and should not qualitatively change the results. We think that it is remarkable that these results are in very reasonable agreement with the $l_{in}$ RIOS computations$^{4,7}$ and in any case the total cross section is in excellent agreement with the quantal $l_{in}$ RIOS and $j_f$ conserving results.

In Fig. 5 we compare the rotational distributions of the forward reactions as found from the forward and reverse computations. We note that for $v_f = 2$ there is a reasonable agreement, although consistently the forward cross sections are larger than the reverse. The discrepancy for $v_f = 3$ is dramatic. Note how the adiabatic barrier restricts the reverse reaction. One is restricted in the reverse reaction to $j_f = 7$. In the forward reaction one can populate much higher $j$ states because of the vibrational boxing. Thus the maximum of the distribution is at higher $j_f$ and the total cross section into $v_f = 3$ is much larger than predicted by the reverse computation.

IV. DISCUSSION

We have shown that there is a qualitative difference between the (reverse) HF($v = 2$) and HF($v = 3$) angular distributions. We have also seen that the HF($v = 3$) cross sections are restricted by the $v = 3$ adiabatic barrier in the exit channel. As shown in Fig. 3, this barrier also effectively limits the accessible $l$ states for $v = 3$ thus forcing the reaction to be essentially collinear. For the $v = 2$ channel this restriction will of course exist at low energies where the saddle point region of the surface dominates. However as energy is increased higher $l$ states contribute and the distribution shifts sideways. The angular momentum restriction may also be discerned from the detailed reaction probability matrices (cf. Table III) where we saw that more rotational states of HH are populated for HF($v = 2$) than for HF($v = 3$).

The reason that the forward quasiclassical computations do not show the sideways peak for $v = 2$ must be associated with the boxing of products. The HF($v = 2$)
angular distribution includes classical trajectories that end up with 3 h vibrational action of HF. These trajectories, according to our analysis, would tend to be backwards scattered, much more than those with 2.5 h vibrational action in HF. Furthermore, because of the transfer of momentum constraint, they are more probable than the 2.5 h trajectories and so will mask any sideways shift. To prove this point, we show in Fig. 7 detailed angular distributions for the forward reaction, but with vibrational action boxed at 0.2 h intervals. Here the trend from backward scattering to sideways scattering as one goes from high \( v \) to low \( v \) is noticeable and in agreement with the reverse computations. Note also the oscillatory structure of the differential cross section when considered as a function of \( v_f \) at fixed angle.

To further strengthen our analysis, we show in Fig. 8 the total reactive cross section for the forward process as a function of final vibrational state but using the 0.2 h boxes. Note that the maximum is at \( v_f = 2.5 \). It is then also not surprising that the forward quasiclassical cross section is larger than approximate quantal results. Quantally, there is a large energetic mismatch between HF(\( v = 2 \)) and HH(\( v = 0 \)). On the other hand, the HF(\( v = 3 \)) state is relatively closed because of the adiabatic barrier. The forward quasiclassical method of course can overcome the mismatch by allowing noninteger actions and so gives cross sections that are probably too large.

The branching ratio into the \( v_f = 3 \) and \( v_f = 2 \) states found from Fig. 8 is 0.34 which is also in better agreement with the reverse computation (cf. Table II). One can also compare the distribution of final \( j_f \) states as found from the forward computation but with 0.2 h vibrational boxes, with the reverse quasiclassical computations (cf. Table IV). This is shown in Fig. 9. Here the distributions have been normalized to one at their maximum. This figure should be compared with Fig. 5. The good agreement found at \( v_f = 3 \) in Fig. 9 is in

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**FIG. 7.** Angular distributions from forward quasiclassical trajectories. Here the final vibrational action is put into 0.2 h action boxes. Note the fine structure of the distributions which is masked in Fig. 4.

**FIG. 8.** Product vibrational distribution for the forward reaction. Note the strong peak of the distribution at \( v_f = 2.5 \) — far from the quantal values of 2.0, 3.0.

**FIG. 9.** Normalized product's rotational distributions within a vibrational manifold. The histograms are from forward quasiclassical trajectories whose final vibrational action is put into 0.2 h action boxes. The solid circles are the results from the reverse computation (cf. Table IV). The distributions are normalized to one at their maximum.
striking contrast to Fig. 5. This again verifies the importance of the exit channel adiabatic barrier.

This analysis then implies that to obtain an accurate approximation to quantal results from quasiclassical trajectories, it is imperative to quantise the initial and final state. Such a method has been suggested by Miller\textsuperscript{27} a decade ago but has not been put into general use because of its expense, although more efficient root searching techniques are being developed.\textsuperscript{27}

More specifically to the FHH system, we have shown that the sideways peak of the HF\((v = 2)\) product angular distribution is a quantal effect in the sense that one must quantise the initial \textit{and} final vibrational states. But seemingly we have shown that the quantal resonance is not the dominating factor leading to the effect, since, of course, Feshbach type resonances do not occur in classical trajectories. This apparently conflicts with the recent analysis of Bowman, Lee, and Ju,\textsuperscript{28} which assumes a direct correlation between the collinear resonance and the sideways peak in the \(v = 2\) distribution. It is plausible though that if these authors would use as input the reverse quasiclassical collinear reaction probabilities\textsuperscript{28} they would also find a sideways peak in the \(v = 2\) angular distribution. However, it is likely that the peak of the distribution would be smaller. In other words, it is reasonable to assume that the shift in the distribution and the magnitude of the shift may be enhanced by the resonance. In fact, comparison of the angular distributions in Figs. 6 and 7 with quantal results obtained from the RIOS approximation (cf. Fig. 4) and the \(j_s\) conserving results shows that the quantal computations do give a larger shift and an enhanced peak.

Since all present 3D quantal approaches are approximate, it is still unclear which is the most accurate. It has been suggested that the \(l_m\) RIOS results are the most reliable since they are the only ones that give total cross sections in agreement with the forward quasiclassical computations.\textsuperscript{6} The \(l_m\) RIOS and \(j_s\) conserving results are smaller by a factor of 2. Our reverse quasiclassical computations suggest, that in fact, the forward (classical) results should be larger than the quantal due to the boxing of the final \((v_f = 3)\) state for which noninteger values of \(v_r\) are much more probable than \(v_r = 3\) (cf. Fig. 8). Finally, the HF\((v = 3)\)/HF\((v = 2)\) branching ratio we find with the reverse computations is in reasonable agreement with the RIOS especially when one considers that tunneling through the adiabatic exit channel barrier should increase the quantal \(v = 3\) cross section relative to the classical) but deviates drastically from the \(j_s\) conserving results.

In summary, we find that one can obtain via quasiclassical trajectory computations, good agreement with quantal approaches, provided that one understands the important effects governing the reaction. It is not yet clear, to what extent the experimental angular distributions of the FHH reaction actually prove the existence of a quantal resonance.

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