Experimental study of the dynamics of D + H₂ reactive and inelastic collisions below 1.0 eV relative energy

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We report the results of state-to-state dynamics experiments on the D + H₂ → HD + H reaction as well as D + H₂ → H₂ + D energy transfer at relative energies of 0.67 and 0.79 eV. Both product state distributions and absolute partial cross sections have been determined, from coherent anti-Stokes Raman scattering (CARS) spectra of the HD and H₂ products recorded under single-collision conditions following pulsed-laser photolysis of DI to generate the D atom reactant. At both energies and for both reactive and inelastic collisions there is a strong dynamical bias against rotational and vibrational excitation of the product. However, at 0.67 eV there is an enhancement of both the relative and absolute yield of HD (ν' = 1), and to a lesser extent H₂ (ν' = 1), the only energetically accessible vibrationally excited product states. This may be the result of a Feshbach resonance at ≈0.65 eV, just above the ν' = 1 threshold energy. Product quantum state distributions from quasiclassical trajectory calculations are in fairly good agreement with the experimental results, except that they do not show the ν' = 1 enhancement at 0.67 eV. However, the partial cross sections from the trajectory calculations are systematically larger than those measured.

I. INTRODUCTION

As the simplest chemical reaction, the hydrogen exchange reaction holds a unique position in chemical dynamics, particularly theoretical chemical dynamics. It has been a testing ground for classical, semiclassical, and approximate quantum mechanical dynamical calculations, and is one of only a few systems for which exact three-dimensional quantum mechanical calculations of the dynamics have been carried out. The lightness of the nuclei in the hydrogen exchange reaction makes quantum effects such as tunneling and dynamical resonances important and observable.

Because of its significance we have chosen to carry out an extensive series of experimental studies on the hydrogen exchange reaction. Originally our experiments focused on the H + D₂ → HD + D isotopic variant of the reaction and the associated rotationally and vibrationally inelastic collision process H + D₂ → D₂ + H, at energies quite far above threshold, ≳1.0 eV, for which many product states are energetically accessible. More recently our experiments have involved the classic H + H₂ → H₂ + H isotopic variant at collision energies between 0.7 and 1.0 eV, where a rich spectrum of dynamical resonances is observed. This publication deals with the remaining easily accessible isotopic variant of the reaction, D + H₂ → HD + H, and the associated D + H₂ → H₂ + D inelastic collisions.

These D + H₂ collisions afford the only opportunity in our experiments to access collision energies not much greater than the reaction threshold. In our H + D₂ experiments collision energies below 0.76 eV are not accessible and for H + H₂ energies below 0.63 eV are not accessible, while for D + H₂ we can get lower than 0.48 eV. These restrictions are kinematic ones associated with the source of the reactant atom in our experiments, photolysis of HI(DI). We cannot produce H or D atoms with lab energies below about 1.0 eV by photolysis of HI or DI, due to limitations imposed by the electronic absorption spectrum of HI(DI). No other photolytic source can yield monoenergetic or nearly monoenergetic H(D) atoms with lab energies this low, so the limitations imposed by the HI(DI) photochemistry are absolute ones. The relative energy in the hydrogen exchange reaction using fast, photolytic hydrogen atoms and a thermal sample of hydrogen molecules is given approximately by

$$E_{\text{rel}} = \left( \frac{\mu}{m_{\text{atom}}} \right) E_{\text{atom}},$$

where \(\mu\) is the reduced mass of the atom + diatom collision pair, \(m_{\text{atom}}\) is the mass of the H(D) atom, and \(E_{\text{atom}}\) is the translational energy of the atom in the laboratory frame. The ratio \(\mu/m_{\text{atom}}\) is 0.8 for H + D₂, 0.67 for H + H₂, and 0.5 for D + H₂, and the 1.0 eV lower limit on \(E_{\text{atom}}\) imposed by the electronic absorption spectrum of HI(DI) yields the lower limits on \(E_{\text{rel}}\) for these reactions.

We describe here results of experimental studies of the D + H₂ reaction at \(E_{\text{rel}} = 0.67\) and 0.79 eV. These energies are not the lowest possible; exploration of the D + H₂ reaction dynamics near threshold will be done in subsequent experiments. The choice of these collision energies was influenced by the results of our recent H + H₂ state-to-state dynamics experiments, which reveal pronounced dynamical resonances, Feshbach resonances, at several relative energies, including 0.70 eV. Resonances are often associated with energetic thresholds for particular product vibrational states. In the H + H₂ and D + H₂ reactions the ν' = 1 thresholds are at collision energies of 0.66 and 0.61 eV respectively [for H₂ (ν = 0, J = 0) reactant]. The opportunity to compare the state-to-state dynamics of D + H₂ → HD + H and H + H₂ → H₂ + H in the vicinity of a dynamical resonance seems particularly appealing. In fact, we do find evidence of a Feshbach resonance in D + H₂ → HD + H as well.

Even if resonance effects were absent, these lower collision energy D + H₂ experiments would be desirable as an...
extension of our previous $E_{rel} > 1.0 \text{ eV H} + \text{D}_2$ studies.\textsuperscript{26–31} These $\text{H} + \text{D}_2$ experiments at collision energies of 0.98, 1.10, and 1.30 eV yielded product state distributions and partial cross sections that are in surprisingly good agreement with the results of quasiclassical trajectory calculations (QCT).\textsuperscript{26–33} Will this agreement between experiment and QCT calculations extend to lower collision energies and other isotopic combinations of the hydrogen exchange reaction? Since we observe in $\text{H}_2$ that appear to be dynamical resonance effects in $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ at $E_{rel} = 0.67 \text{ eV}$ the quasiclassical trajectory calculations should not provide a good description of the dynamics at this energy. In fact, there is reasonable agreement between the QCT calculations and experiment for the relative population distributions at 0.79 eV, while at 0.67 eV where the resonance effect appears, the QCT-experiment agreement is not so good, particularly for the ratio of $\nu' = 1$ to $\nu' = 0$. Overall the QCT calculations do not give as good agreement with experiment as they did for $\text{H} + \text{D}_2$ at higher collision energies.

In the next section we give a brief description of the experimental apparatus and method used to do these experiments, while Sec. III presents the results of the experiments. In Sec. IV we compare these experimental results with QCT calculations, with our results from experiments with other isotopic variants of the hydrogen exchange reaction, and with the results of crossed molecular beam experiments of $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ at relative energies between 0.85 and 1.20 eV.\textsuperscript{34,35} Our conclusions about the dynamics of $\text{D} + \text{H}_2$ collisions are summarized in Sec. V.

II. EXPERIMENT

As in our previous $\text{H} + \text{D}_2$ and $\text{H} + \text{H}_2$ state-to-state dynamics experiments we use coherent anti-Stokes Raman scattering (CARS) spectroscopy to measure the rotational and vibrational state distributions of the reactive HD and inelastic $\text{H}_2$ products of $\text{D} + \text{H}_2$ collisions under single-collision conditions. The D atoms are generated by pulsed-laser photolysis of DI. Since the experimental apparatus and methodology used here have been described extensively in Refs. 27 and 28, we will give only a brief description of the experiment.

The reactions are carried out in a 5 cm long, 3 mm i.d. open-ended glass sample cell, suspended in a 150 cm long by 7.5 cm i.d. glass cell. An approximately equimixture of DI/H$_2$ at 4–5 Torr total pressure flows through the sample cell at a rate (0.20 Torr $\ell \text{s}^{-1}$) sufficient to replenish the reaction mixture between laser shots at the 10-pulse-per-second repetition rate of the pulsed lasers. A stream of argon enters the gas cell near the laser beam entrance and exit windows at the ends of the gas cell, to prevent the buildup of species on the windows. The total gas pressure is 11–12 Torr (7.0 Torr Ar plus the 4–5 Torr equimixture of DI/H$_2$). The DI used in the experiments is synthesized by the reaction of D$_2$ with I$_2$ over a platinum catalyst.\textsuperscript{36} A 2 $\ell \text{atm}$ sample was made a few hours ahead of the time the experiment was done. The purity of the DI sample was determined from DI and HI CARS spectra, and found to be greater than 95%.

A 5 ns FWHM UV laser pulse dissociates the DI in the mixture, producing translationally hot deuterium atoms. Two 5 ns FWHM visible laser pulses probe the $\text{H}_2$ and HD products 5 ns after the UV photolysis pulse, generating a CARS signal from the products. The DI photolysis wavelengths used in the present experiments are 266 and 280 nm, giving $\text{D} + \text{H}_2$ collision energies of 0.79 and 0.67 eV. The frequency-quadrupled output of a Nd:YAG laser provides the 266 nm light, while the frequency-doubled output of a tunable dye laser is the source of the 280 nm light. CARS\textsuperscript{37} is a nonlinear process that requires two laser frequencies, the pump, $\omega_p$, and a second, the Stokes, $\omega_s$. In our experiments $\omega_p$ is fixed (Nd:YAG second harmonic), while $\omega_s$ (tunable Nd:YAG-pumped dye laser) is scanned to give the CARS spectrum. The CARS signal appears at the anti-Stokes frequency, $\omega_{as} = 2\omega_p - \omega_s$, where $\omega_s = \omega_p - \omega_i$, is the Raman transition frequency. Edge filters and a double monochromator spectrally and spatially separate $\omega_{as}$ from $\omega_p$ and $\omega_s$. The CARS signal is detected by a photomultiplier tube, processed by a boxcar integrator, digitized, and recorded by a microcomputer.

The mean time between hard-sphere, elastic $\text{D} + \text{H}_2$ collisions is about 6 ns under the conditions of these experiments. This is calculated using a hard-sphere collision cross section of 9 Å$^2$ for $\text{D} + \text{H}_2$. Previous work done under similar conditions for $\text{H} + \text{D}_2$ at $E_{rel} = 1.30 \text{ eV}$ showed no discernible difference among HD product spectra taken with the CARS probe pulses delayed with respect to the photolysis pulse by less than 10 ns.\textsuperscript{27} Thus, the present experiments, done with a 5 ns delay time, correspond effectively to single-collision conditions.

III. RESULTS

Figure 1 shows the vibrational Q-branch spectrum of the rotationally and/or vibrationally excited $\text{H}_2$ product formed by inelastic $\text{D} + \text{H}_2$ collisions at $E_{rel} = 0.79 \text{ eV}$. The thermally populated reactant $\nu = 0, j = 4$ state peak, and the product peaks for $\nu' = 0, j' = 4, 5, 6, 7, 8$, and $\nu' = 1, j' = 1$ are plotted. The higher intensity for odd-j$'$ peaks compared with that for even-j$'$ peaks is a consequence of the different nuclear spin degeneracies, namely 3 for odd $j$ and 1 for even $j$.

Figure 1. The vibrational Q-branch CARS spectrum of the $\text{H}_2$ product from $\text{D} + \text{H}_2$ collisions at $E_{rel} = 0.79 \text{ eV}$.
The vibrational Q-branch spectrum of HD product formed by reactive D + H₂ collisions at the same energy is pictured in Fig. 2. The HD \( v' = 0, j' = 1-9 \) and \( v' = 1, j' = 1-6 \) product peaks are illustrated.

Since all the peaks in the spectra are well resolved, the CARS signal is given by

\[
S(\omega_m) = \frac{\hbar}{\omega_m} (\Delta N)^2 (d\sigma/d\Omega)^2 \times \int g(\omega;\omega_m) F_2 [(f')^2 + (f'^*)^2] d\omega + 2\frac{\hbar}{\omega_m} (\Delta N) (d\sigma/d\Omega) \chi'' \times \int g(\omega;\omega_m) F_2 f'^* d\omega + (\chi''')^2 \int g(\omega;\omega_m) F_2 d\omega
\]

where \( \omega_m \) and \( \omega \) are the anti-Stokes and Stokes laser frequencies, \( d\sigma/d\Omega \) is the Raman cross section for the transition, \( g(\omega;\omega_m) \) is the CARS laser line shape function centered at \( \omega_m \), \( F_2 \) is a factor dependent on the CARS laser frequencies and the focusing conditions, and \( f' \) and \( f'^* \) are line shape functions of the real and imaginary parts of the third-order optical hyperpolarizability. Analysis of the spectra is done by generating \( S(\omega_m) \) from Eq. (2) for various \( \Delta N \), and comparing these with the experimental \( S(\omega_m) \) to determine the correct \( \Delta N \). From these \( \Delta N(v', j') = N(v', j') - N(v' + 1, j') \) we derive the \( N(v', j') \) by setting \( N(v', j') \) equal to zero for those states not energetically accessible.

Table I lists the relative populations derived from such an analysis for the H₂ and HD products of D + H₂ collisions at relative energies of 0.79 and 0.67 eV. The inelastic population distributions at both energies fall rapidly with increasing \( j' \). For the inelastic H₂ product only 1 state in \( v' = 1 \) had a large enough population to be detected. Only an upper limit can be placed on the relative populations of the H₂ product in \( v' = 1, j' = 3 \), namely 0.7 at 0.67 and 0.5 at 0.79 eV. It is difficult to establish even upper limits on the H₂ \( v' = 1, j' = 0 \) and 2 populations, as a consequence of even-\( j' \) levels having a spin degeneracy three times smaller than the odd \( j' \) levels. However, the absolute amount of H₂(\( v' = 1 \)) is not really small, because the absolute partial cross section for the state is larger than the partial cross section for any \( v' = 1 \) reactive product state. The CARS spectral region of the inelastic collision products has a large background contribution from nearby thermal reactant H₂ transitions. Thus, the sensitivity of the experiment for inelastic product is less than that for the reactive product, for which the CARS spectral region has a negligible background contribution from reactant H₂. At the higher collision energy H₂ states up to \( v' = 6 \) are energetically allowed, while at the lower energy the limits are \( v' = 0, j' = 9 \), and \( v' = 1, j' = 4 \). At the 0.79 eV collision energy HD states up to \( v' = 0, j' = 12 \) and \( v' = 1, j' = 8 \) are energetically accessible, while at 0.67 eV states up to \( v' = 1, j' = 11 \) and \( v' = 1, j' = 6 \) are allowed. The reactive population distributions are plotted in Figs. 3 and 5, and the inelastic population distributions in Figs. 4 and 6, as points with ± one standard deviation error bars. The reactive population distributions at both energies show relatively broad rotational distributions that don’t drop off as rapidly as their inelastic counterparts.

Our experiments also provide a measurement of the absolute cross sections for these reactions, since absolute densities of both the reactants and the diatomic product can be made using CARS. The cross sections are given by

\[
\sigma(v', j') = \frac{\Delta N(v', j')}{(D[H_2])f_{rel}}
\]

![FIG. 2. The vibrational Q-branch CARS spectrum of the HD product from D + H₂ collisions at \( E_{rel} = 0.79 \) eV.](image-url)
The relative velocities are 1.25 $\times 10^6$ cm s$^{-1}$ for $E_{rel} = 0.79$ eV, 1.14 $\times 10^6$ cm s$^{-1}$ for $E_{rel} = 0.67$ eV, and 2 $\times 10^6$ cm s$^{-1}$ for $E_{rel} = 0.32$ eV. The number density of deuterium atoms, [D], is given by

$$[D] = [DI] f_{photo} f_{lec},$$

where [DI] is the DI number density, $f_{photo}$ is the fraction of DI dissociated by the UV photolysis pulse (determined from the observed depletion of the DI CARS signal with the addition of the UV pulse), and $f_{lec}$ is the quantum yield for the production of D + I($^2P_{3/2}$). The quantity $f_{lec}$ is less than unity because dissociation of DI can lead to D + I($^2P_{1/2}$) or D + I($^2P_{3/2}$). For dissociation at 266 nm these two dissociation channels produce D atoms that give $E_{rel}$ of 0.79 and 0.32 eV, respectively, while dissociation at 280 nm gives $E_{rel}$ of

\[ \sigma(v', j') = [\text{HD}(v', j')] / ([D][H_2] \Delta \nu_{rel}), \]  

where $[X]$ indicates a particle number density, $\Delta \nu$ is the time between the UV photolysis pulse and the CARS probe pulses, and $\nu_{rel}$ is the D + H$_2$ relative velocity. The collision velocity $\nu_{rel}$ is given by

$$\nu_{rel} = \sqrt{2E_{rel}/\mu},$$

where $E_{rel}$ is the collision energy and $\mu$ is the reduced mass of D + H$_2$. The relative velocities are 1.25 $\times 10^6$ cm s$^{-1}$ for $E_{rel} = 0.79$ eV and 1.14 $\times 10^6$ cm s$^{-1}$ for $E_{rel} = 0.67$ eV. The time delay $\Delta \nu$ is 5 ns. The number density of the H$_2$ reactant is known from a simple pressure measurement. Measurement of the CARS signals from the H$_2$ reactant calibrates the CARS spectral intensities and permits absolute measurement of the H$_2$ and HD product number densities.

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0.67 and 0.20 eV, respectively. For 266 nm photolysis of DI the quantum yield is 0.74 for D + I(2P\(3/2\)) and 0.26 for D + I(2P\(1/2\)). Photolysis of DI at 280 nm leads to greater than 95% production of the D + I(2P\(3/2\)) channel. The collision energies of the slower D atoms from the D + I(2P\(3/2\)) channel, 0.32 and 0.20 eV, are below the reaction threshold, and therefore of no significance for the exchange reaction. These slower D atoms produced in 266 nm DI photolysis can, however, contribute to inelastic, particularly rotationally inelastic, collisions, and our measured H\(_2\) product population distributions must contain some contribution from them. However, even if the excitation cross section in D + H\(_2\) collisions at 0.32 eV were to be as large as at 0.79 eV, the slower D atoms could contribute no more than 17% of the inelastic H\(_2\) product. For 0.32 eV collision energy H\(_2\) states only up to \(\nu' = 0, j' = 6\) are accessible.

The absolute partial cross sections we derive are listed in Tables II and III. The additional measurements needed to calculate the absolute partial cross sections lead to larger uncertainty in them in the relative populations. The major sources of the additional uncertainty are associated with measurement of the degree of DI photolysis, measurement of the pressure of the DI, and uncertainty in the time delay.

### Table II. Absolute partial cross sections for D + H\(_2\) \(\rightarrow\) H\(_2\)(\(\nu', j'\)) + D at 0.67 and 0.79 eV collision energy.

<table>
<thead>
<tr>
<th>(\nu', j')</th>
<th>(E_{\text{rel}} = 0.67) eV</th>
<th>(E_{\text{rel}} = 0.79) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 4</td>
<td>0.36 (\pm) 0.13</td>
<td>0.37 (\pm) 0.12</td>
</tr>
<tr>
<td>0, 5</td>
<td>0.21 (\pm) 0.07</td>
<td>0.20 (\pm) 0.06</td>
</tr>
<tr>
<td>0, 6</td>
<td>0.16 (\pm) 0.05</td>
<td>0.11 (\pm) 0.04</td>
</tr>
<tr>
<td>0, 7</td>
<td>0.16 (\pm) 0.06</td>
<td>0.10 (\pm) 0.03</td>
</tr>
<tr>
<td>0, 8</td>
<td>\ldots</td>
<td>0.08 (\pm) 0.03</td>
</tr>
<tr>
<td>1, 1</td>
<td>0.06 (\pm) 0.02</td>
<td>0.04 (\pm) 0.015</td>
</tr>
</tbody>
</table>

Of particular note with regard to these partial cross sections is the fact that both the HD and H\(_2\) \(\nu' = 1\) product cross sections are larger at the lower of the two collision energies. For the inelastic product the difference between the \(\sigma(\nu' = 1)\) at the 0.67 and 0.79 eV collision energies is within experimental uncertainty, but the \(\sigma(\nu' = 1)\) difference is quite large and definitely significant for the reactive product. The enhancement of \(\nu' = 1\) HD production relative to \(\nu' = 0\) HD is also clearly evident in the population distributions of Table I and Figs. 3 and 5. We believe this is evidence for a Feshbach resonance in D + H\(_2\) collisions, a contention discussed more fully in the next section.

We have calculated the fractional energy disposal for the product energy distributions in the reactive HD product of D + H\(_2\) collisions at the two energies studied. The results are listed in Table IV, together with the energy disposal that characterizes the results of some of our previous experiments with other isotopic variants of the hydrogen exchange reaction. In all cases 69%–84% of the energy appears in translation, 8%–25% is in rotation, and 2%–10% is in vibration. The energy disposal for D + H\(_2\) \(\rightarrow\) HD + H shows the considerable enhancement of product vibration at the lower of the two collision energies studied, where we believe a Feshbach resonance is operative. Feshbach resonances in H + p-H\(_2\) at 0.70 and 1.00 eV collision energy also are accompanied by an increase in \(J_{\text{vm}}\) relative to off-resonance collision energies 0.79 and 1.10 eV.

While the fractional energy disposal provides a convenient and simple description of the product rotational and vibrational distributions, a linear surprisal analysis\(^40\)–\(^42\) provides a more useful parametrization of these distributions. The surprisal analysis involves comparing the observed product state distributions with a common reference distribution, a statistical distribution in which all product states are equally probable. The provision of a common reference "frame" allows direct and meaningful comparison of the H + H\(_2\) reaction dynamics at different energies and for different isotopic variants of the reaction, helping to identify

### Table III. Absolute partial cross sections for D + H\(_2\) \(\rightarrow\) HD(\(\nu', j'\)) + H at 0.67 and 0.79 eV collision energy.

<table>
<thead>
<tr>
<th>(\nu', j')</th>
<th>(E_{\text{rel}} = 0.67) eV</th>
<th>(E_{\text{rel}} = 0.79) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 1</td>
<td>0.097 (\pm) 0.033</td>
<td>0.064 (\pm) 0.022</td>
</tr>
<tr>
<td>0, 2</td>
<td>0.100 (\pm) 0.034</td>
<td>0.084 (\pm) 0.028</td>
</tr>
<tr>
<td>0, 3</td>
<td>0.102 (\pm) 0.035</td>
<td>0.089 (\pm) 0.030</td>
</tr>
<tr>
<td>0, 4</td>
<td>0.112 (\pm) 0.038</td>
<td>0.097 (\pm) 0.033</td>
</tr>
<tr>
<td>0, 5</td>
<td>0.087 (\pm) 0.029</td>
<td>0.090 (\pm) 0.030</td>
</tr>
<tr>
<td>0, 6</td>
<td>0.078 (\pm) 0.027</td>
<td>0.097 (\pm) 0.033</td>
</tr>
<tr>
<td>0, 7</td>
<td>0.051 (\pm) 0.021</td>
<td>0.074 (\pm) 0.025</td>
</tr>
<tr>
<td>0, 8</td>
<td>\ldots</td>
<td>0.077 (\pm) 0.026</td>
</tr>
<tr>
<td>0, 9</td>
<td>\ldots</td>
<td>0.050 (\pm) 0.017</td>
</tr>
<tr>
<td>1, 1</td>
<td>0.021 (\pm) 0.007</td>
<td>0.009 (\pm) 0.003</td>
</tr>
<tr>
<td>1, 2</td>
<td>0.024 (\pm) 0.008</td>
<td>0.009 (\pm) 0.003</td>
</tr>
<tr>
<td>1, 3</td>
<td>0.026 (\pm) 0.009</td>
<td>0.012 (\pm) 0.004</td>
</tr>
<tr>
<td>1, 4</td>
<td>0.023 (\pm) 0.008</td>
<td>0.016 (\pm) 0.005</td>
</tr>
<tr>
<td>1, 5</td>
<td>\ldots</td>
<td>0.008 (\pm) 0.003</td>
</tr>
<tr>
<td>1, 6</td>
<td>\ldots</td>
<td>0.007 (\pm) 0.002</td>
</tr>
</tbody>
</table>

### Table IV. Energy disposal in three isotopic variants of the hydrogen exchange reaction.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E_{\text{rel}})</th>
<th>(f_{\text{trans}})</th>
<th>(f_{\text{rot}})</th>
<th>(f_{\text{vm}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>D + H(_2) (\rightarrow) HD + H(_2)</td>
<td>0.67 eV</td>
<td>0.71</td>
<td>0.19</td>
<td>0.10</td>
</tr>
<tr>
<td>D + H(_2) (\rightarrow) HD + H(_2^*)</td>
<td>0.79 eV</td>
<td>0.70</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td>H + D(_2) (\rightarrow) HD + D(_2^*)</td>
<td>0.98 eV</td>
<td>0.73</td>
<td>0.21</td>
<td>0.06</td>
</tr>
<tr>
<td>H + p-H(_2) (\rightarrow) H(_2) + H</td>
<td>1.10 eV</td>
<td>0.74</td>
<td>0.22</td>
<td>0.04</td>
</tr>
<tr>
<td>H + p-H(_2) (\rightarrow) H(_2) + H(_2^*)</td>
<td>1.30 eV</td>
<td>0.69</td>
<td>0.24</td>
<td>0.07</td>
</tr>
</tbody>
</table>

\(^a\)The fraction of the total available energy in product translation.

\(^b\)The fraction of the total available energy in product rotation.

\(^c\)The fraction of the total available energy in product vibration.

\(^d\)This work.

\(^e\)References 27 and 28.

\(^f\)References 24 and 25.
The utility of this information theory approach has been the bias of the reaction. This is the principal advantage of the surprisal analysis, and the primary reason for our use of it.

The statistical, or prior, distribution that provides the common reference in the surprisal analysis is, for an atom plus diatom reaction, given by

$$P_{0}(v', j') = \frac{(2j' + 1)}{\sum_{v,j'} (2j' + 1)} (E - E_v - E_{j'})^{1/2},$$

(7)

where $E$ is the total energy, and $E_v$ and $E_{j'}$ are the vibrational and rotational energies of the diatom. $P_{0}(v', j')$ is simply the number of states with quantum numbers $v'$ and $j'$, divided by the total number of product states energetically accessible. The product distributions are related to this prior distribution via the linear surprisal parameters, $\alpha_v$ and $\theta_{j'}$, for the vibration and rotation, respectively, of the product diatom,

$$P(v', j') = P_{0}(v', j') \exp(-\alpha_v - \lambda_{0} f_v - \theta_{j'} g_v).$$

(8)

The parameters $f_v$ and $g_v$ are the fractions of the energy in vibration and rotation, $f_v = E_v/E$ and $g_v = E_v/(E - E_v)$, and $\alpha_v$ is a scale factor.

The prior distribution used in this formulation lacks the constraint of conservation of total angular momentum. While in principle this is a serious deficiency, in practice it does not remove the utility of the linear surprisal description. However, as a consequence of this omission, the value of the rotational surprisal parameter $\theta_{j'}$ may reflect the angular momentum conservation constraint that is lacking in the statistical (reference) distribution. For our purposes any such influence on $\theta_{j'}$ does nothing to diminish its usefulness, since we invoke it simply as a convenient parametrization of the product rotational state distribution, a parametrization that allows systematic intercomparison of the rotational state distributions in the various experiments we have carried out on the hydrogen exchange reaction. That is, we interpret the surprisal parameters largely in terms of their values relative to one another.

Linear least-squares fitting of the surprisal function of Eq. (8) to our H$_2^+$ and HD product quantum state distributions yields the solid lines shown in Figs. 3–6. In all cases the simple linear surprisal function provides a good description of the measurements. For the inelastic product of D + H$_2$ collisions at $E_{rel} = 0.67$ and 0.79 eV we find $\theta_{j'} = 5.2 \pm 1.10$ and $4.4 \pm 0.2$ for $v' = 0$. While the linear rotational surprisal function describes the measured inelastic H$_2$ product distributions reasonably well, the use of the surprisal function to extrapolate the product populations to higher and lower $j'$ than observed is not recommended. There are simply too few measured H$_2^+$ $(v' = 0,j')$ populations to yield a $\theta_{j'}$ that we can be confident enough of to allow such extrapolation. For D + H$_2$ reactive collisions at $E_{rel} = 0.79$ eV we find linear rotational surprisal parameters $\theta_{j'} = 2.5 \pm 0.1$ for $v' = 0$ and $\theta_{j'} = 2.0 \pm 0.3$ for $v' = 1$. At $E_{rel} = 0.67$ eV we find $\theta_{j'} = 3.8 \pm 0.50$ for $v' = 0$ and $2.0 \pm 0.4$ for $v' = 1$. The inelastic D + H$_2$ collisions at both energies show more bias against rotation than the reactive D + H$_2$ collisions. We have also found this behavior for the H + p − H$_2$ and H + D$_2$ collisions that we have studied previously.

The vibrational surprisal parameters that best describe the inelastic data are $\lambda_v = 0.74 \pm 0.2$ at 0.67 eV and $\lambda_v = 1.3 \pm 0.2$ at 0.79 eV. However, since we have been able to observe product in only a single rotational state of $v' = 1$, the vibrational state distribution of the H$_2$ product is not well determined. For reactive D + H$_2$ collisions the larger number of $v' = 1$ product rotational states observed makes it easier to determine $\lambda_v$. For 0.67 eV we find $\lambda_v = 0.6 \pm 0.2$ while at 0.79 eV this is $2.2 \pm 0.2$. Note the significant decrease in $\lambda_v$ at the lower collision energy, reflecting a relaxation of the dynamical bias against product vibrational excitation. Since the linear surprisal function provides a good description of our HD product quantum state distributions, we can use the surprisal function to determine $N(v', j')$ and $\sigma(v', j')$ for those $v', j'$ states not actually observed in the experiment. This allows us to compute a total reaction cross section, summed over $v'$ and $j'$, even though there are missing states in our measurements. We find that the total cross section at both 0.67 and 0.79 eV relative energies is $0.81 \pm 0.35$ Å$^2$. The $N(v', j')$ represented by the linear surprisal functions are also used to calculate the fractional energy disposal data given in Table IV.

IV. DISCUSSION

A. Dynamical resonance behavior

As the collision energy is lowered from $E_{rel} = 0.79$ eV to $E_{rel} = 0.67$ eV the energy available to the products of the D + H$_2$ → HD + H reaction goes down, and it would be reasonable to expect the product distributions to shift to lower $v', j'$ states at the lower collision energy. The H$_2$ potential energy surface is a minimum barrier for collinear geometry, and the barrier height increases rapidly with decreasing H−H−H angle, from about 0.40 eV for 180° to about 1.3 eV for 90°. Therefore, as the collision energy is decreased the reactive collisions become more constrained to near-collinear geometries and smaller impact parameters, both of which should favor less product rotational excitation. The predominant vibrational adiabaticity for the hydrogen exchange reaction also suggests decreasing vibrational excitation with decreasing collision energy.

The product distributions in Figs. 3 and 5 show the expected trend for rotational excitation, but the vibrational excitation at the lower collision energy is greater than that in the higher collision energy experiment. This is apparent in the $\sigma(v', j')$ partial cross sections as well. This type of behavior could indicate oscillatory, or resonance like, $\sigma(v')$ partial cross sections. The increase in the relative, as well as the absolute, yield of the HD $(v' = 1)$ product of the D + H$_2$ reaction that accompanies a small decrease in the relative energy is the most significant observation of this study, for we believe this to be the result of a dynamical resonance in the reaction at about 0.65 eV. There is evidence to suggest that this interpretation is correct.

A Feshbach resonance in any isotopic variant of the hydrogen exchange reaction is expected just above the energetic threshold for the $v' = 1$ product. Recent calculations by Webster and Light indicate that the threshold for the
D + H$_2$($v^\prime = 0$) → HD($v^\prime = 1$) + H reaction is at 0.61 eV relative energy. These calculations also show a peak in the $v^\prime = 1$ cross section and a dip in the $v^\prime = 0$ cross section at $\approx 0.67$ eV relative energy, which is likely to be the result of the expected Feshbach resonance. The $n = 1$ vibrationally adiabatic potential energy surface$^{47}$ for DH$_2$ shows a well that could support the quasibound state necessary to produce the Feshbach resonance internal excitation state. In our previous experiments on H + H$_2$ we found a strong Feshbach resonance at 0.70 eV collision energy, about 0.04 eV above the $v^\prime = 1$ product threshold, almost exactly where it was predicted theoretically.$^{9-11,48-51}$ The behavior expected for a Feshbach resonance just above the $v^\prime = 1$ product threshold—an enhancement in the $v^\prime = 1$ cross section—is precisely what we observe for both D + H$_2$ and H + H$_2$. Of course, quantum coupled channel calculations also predict a decrease in the $v^\prime = 0$ product cross section at the resonance, and this we do not observe, either for D + H$_2$ or H + H$_2$. However, these calculations have been carried out only for $J = 0$ total angular momentum,$^{7-11}$ and, for H + H$_2$, for selected $J \leq 2$. 

We believe that it is possible to observe the Feshbach resonances that occur just above a particular product vibrational state threshold in the hydrogen exchange reaction because there are only a few partial waves contributing to the near-threshold product vibrational state. As a consequence, the partial wave sum is not so extensive as to wash out the resonance. However, for the reaction to produce lower vibrational states, which are already far above threshold, there are undoubtedly many partial waves contributing and the partial wave sum does apparently wash out the resonance effects. Some evidence to support this view comes from an examination of the rotational distributions of the HD($v^\prime = 1$) product of the D + H$_2$($v = 0$) reaction at 0.79 and 0.67 eV, shown in Table III. The resonance enhancement appears to occur primarily in the lower rotational states of $v^\prime = 1$. To the extent that there is angular momentum coupling between the reactant orbital angular momentum and the product rotational angular momentum, this observation would suggest that it is only partial waves of low orbital angular momentum that are contributing significantly to the resonance.

The increase in the D + H$_2$($v^\prime = 1$) reactive cross section between 0.79 and 0.67 eV is accompanied by a similar, but smaller increase in the $v^\prime = 1$ inelastic cross section. As the data in Tables I and II show, the 33% increase in the relative cross section for H$_2$($v^\prime = 1$), is just barely significant, but, due to the larger uncertainties, this same percent increase is not statistically significant in the absolute partial cross section. Our evidence of the effect of the resonance on the inelastic cross section is thus much weaker than that for the effect on the reactive cross section. However, the effect we do see is consistent with the expectation that this particular Feshbach resonance should enhance the production of both HD($v^\prime = 1$) and H$_2$($v^\prime = 1$) in D + H$_2$($v = 0$) collisions. The enhancement of H$_2$($v^\prime = 1$) should probably be less than that for HD($v^\prime = 1$), because the barrier to decay of the DH$_2$ quasi-bound state is greater for D + H$_2$($v^\prime = 1$) products than for H + HD($v^\prime = 1$) products as a result of the greater vibrational energy of H$_2$($v^\prime = 1$).

The Feshbach resonances result from excitation of the transition state to excited states of the vibrational degrees of freedom perpendicular to the reaction coordinate. The particular resonance that should occur just above the $v^\prime = 1$ product threshold has been assigned to the first excited state of the symmetric stretch motion in the [H$_2$]$^1$ transition state.$^{46-51}$ In the [DH$_2$]$^1$ transition state this resonant state may involve a similar vibrational motion, although it could no longer be called a symmetric stretch, because of the reduced symmetry. In any case, this vibrationally excited transition state can decay to products or to reactants, so its production should enhance both the vibrationally nonadiabatic reactive scattering and the inelastic scattering. There are no quantum calculations on the inelastic collisions of D + H$_2$ that we are aware of, at least no calculations at relative energies around 0.6–0.8 eV, where the Feshbach resonance appears to be. Consequently, there are no theoretical predictions about the relative effect of the resonance on the $v^\prime = 1$ inelastic and reactive cross sections. However, for H + H$_2$ recent coupled channel calculations for $J = 0$ total angular momentum by Hipes and Kuppermann$^{11}$ show an enhancement of both the reactive $v^\prime = 1$ transition probability and the inelastic $v^\prime = 1$ transition probability. In fact this is what we observe in our H + H$_2$ experiments.$^{24,25}$

### B. Angular momentum coupling

Table V summarizes the rotational surprisal parameters in the product distributions for some of the experiments we have carried out for three isotopic combinations, H + p-H$_2$, H + D$_2$, and D + H$_2$, in these hydrogen atom–hydrogen molecule collisions. In all of the systems and at all the energies we have studied there is a relatively strong and consistent bias against rotational excitation, as indicated by the positive rotational surprisal parameters in Table V. However, there is also a difference in the degree of this bias. The

### TABLE V. Rotational surprisal parameters for collisions of hydrogen atoms with hydrogen molecules.

<table>
<thead>
<tr>
<th>Collision type</th>
<th>$E_{rel}$</th>
<th>$v^\prime$</th>
<th>Reactive</th>
<th>Inelastic</th>
</tr>
</thead>
<tbody>
<tr>
<td>D + H$_2$</td>
<td>0.67 eV</td>
<td>$v^\prime = 0$</td>
<td>3.8</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$v^\prime = 1$</td>
<td>2.0</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>0.79 eV</td>
<td>$v^\prime = 0$</td>
<td>2.5</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$v^\prime = 1$</td>
<td>2.0</td>
<td>...</td>
</tr>
<tr>
<td>H + D$_2$</td>
<td>0.98 eV</td>
<td>$v^\prime = 0$</td>
<td>3.5</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$v^\prime = 1$</td>
<td>3.5</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>1.10 eV</td>
<td>$v^\prime = 0$</td>
<td>3.4</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$v^\prime = 1$</td>
<td>3.0</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>1.30 eV</td>
<td>$v^\prime = 0$</td>
<td>3.0</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$v^\prime = 1$</td>
<td>3.0</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$v^\prime = 2$</td>
<td>...</td>
<td>6.9</td>
</tr>
<tr>
<td>H + H$_2$</td>
<td>0.70 eV</td>
<td>$v^\prime = 0$</td>
<td>10.8</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>0.79 eV</td>
<td>$v^\prime = 0$</td>
<td>7.6</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>1.00 eV</td>
<td>$v^\prime = 0$</td>
<td>5.1</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>1.10 eV</td>
<td>$v^\prime = 0$</td>
<td>5.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>
bias against rotational excitation follows the order \(H + p\cdot\text{H}_2 > H + \text{D}_2 > \text{D} + \text{H}_2\). The extent of the bias against rotational excitation for a particular isotopic combination is fairly constant over the somewhat limited energy range of our experiments. For example, for \(H + \text{D}_2 \rightarrow \text{HD} + \text{D}\) at relative energies between 0.98 and 1.30 eV, the rotational surprisal parameters are in the range of 3.0–3.5. For \(H + p\cdot\text{H}_2 \rightarrow \text{o-H}_2 + \text{H}\) reaction over the same energy regime the rotational surprisal parameters range from 5.0 to 5.5, while at lower collision energies, around 0.75 eV, the rotational surprisal parameters are 8 to 11. At these lower collision energies the \(D + \text{H}_2\) system shows less bias against rotational excitation than the other two isotopic combinations. \(D + \text{H}_2 \rightarrow \text{HD} + \text{H}\) has rotational surprisal parameters from 2.0 to 3.8 with three of four between 2.0 and 2.5.

The rotational surprisal parameters should not be over interpreted. Some of the difference among the \(\theta_i\) values for the \(\text{H} + p\cdot\text{H}_2\), \(\text{H} + \text{D}_2\), and \(\text{D} + \text{H}_2\) systems is certainly a consequence of the different total angular momenta in these systems. Since the surprisal analysis uses a prior distribution that is not constrained by conservation of total angular momentum, two systems with identical dynamics will give different \(\theta_i\) if they have different total angular momenta. We can estimate the total angular momenta in these collisions, based on our measurements of the total reaction cross sections, and gauge the importance of the total angular momentum constraint.

For the \(\text{H}_2\) and \(\text{D}_2\) reactants at room temperature \(\langle j' \rangle\) is only 1 or 2, so the total angular momentum \(J\) is dominated by the reactant orbital angular momentum \(l\), i.e., \(J \approx l\). The orbital angular momentum can be related to the total reaction cross section by the classical relations \(l = \mu v_{\text{rel}} b\) and \(\sigma = \pi b^2\), giving

\[
J \approx l = \mu (2E_{\text{rel}}/\mu)^{1/2} (\sigma/\pi)^{1/2} = (2/\pi)^{1/2} (\mu E_{\text{rel}} \sigma)^{1/2}.
\]

At a given energy the reaction cross sections are in the order \(\sigma(D + \text{H}_2) > \sigma(H + \text{H}_2) > \sigma(H + \text{D}_2)\) as a consequence of zero-point energy differences, while \(\mu(D + \text{H}_2) > \mu(H + \text{D}_2) > \mu(H + \text{H}_2)\). Thus, the total angular momentum available in the \(\text{D} + \text{H}_2\) reaction is greater than in the other two isotopic variants, and we expect this reaction to give "hotter" rotational distributions than the other two. However, the rotational distributions we measure do not have \(\langle j' \rangle\) that scale simply as \((\mu E_{\text{rel}} \sigma)^{1/2}\), and the rotational surprisal parameters do reflect changing dynamics in the hydrogen exchange reaction with changes in isotopes.

The same trend in the bias against rotational excitation is found in the inelastic collisions as in the reactive collisions. For a given isotopic variant the bias against product rotational excitation is generally stronger for inelastic than for the reactive collisions. Comparing the \(\theta_i\) for the inelastic collisions of the different isotopic variants we find again \(H + p\cdot\text{H}_2 > H + \text{D}_2 > D + H_2\).

C. Comparison with classical trajectory calculations

In Figs. 7 and 8 we compare the product quantum state distributions for \(\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}\) that we have measured with state distributions from the QCT calculations of Blais and Truhlar.\(^{52}\) The QCT calculations were carried out at several relative energies, but not at the 0.67 or 0.79 eV energies of our experiments. In order to make comparison with the experimental results we have linearly interpolated and extrapolated the 0.70 and 0.85 eV data of Blais and Truhlar. These are the two energies at which the calculations have been done that are closest to the energies of the experiments. In order to make the comparison of relative population distributions shown in Figs. 7 and 8 meaningful, we scale the QCT data such that \(\sum j' N(v', j')\) is the same for it and the experimental data.

Comparing relative population distributions the QCT results are in almost as good agreement with experiment for \(\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}\) at these relatively low collision energies as they are\(^{26-33}\) for \(\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}\) at higher collision energies. Note that at 0.79 eV the calculations give \(j'_{\text{vib}}\)
TABLE VI. Absolute partial cross sections for D + H₂ → HD (v', j') + H at 0.79 eV collision energy.

<table>
<thead>
<tr>
<th>v', j'</th>
<th>Experiment</th>
<th>QCT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 0</td>
<td>0.056</td>
<td>0.178</td>
</tr>
<tr>
<td>0, 1</td>
<td>0.048</td>
<td>0.0523</td>
</tr>
<tr>
<td>0, 2</td>
<td>0.084</td>
<td>0.0669</td>
</tr>
<tr>
<td>0, 3</td>
<td>0.089 ± 0.030</td>
<td>0.1160</td>
</tr>
<tr>
<td>0, 4</td>
<td>0.097 ± 0.033</td>
<td>0.1390</td>
</tr>
<tr>
<td>0, 5</td>
<td>0.090 ± 0.030</td>
<td>0.1570</td>
</tr>
<tr>
<td>0, 6</td>
<td>0.097 ± 0.033</td>
<td>0.1660</td>
</tr>
<tr>
<td>0, 7</td>
<td>0.074 ± 0.025</td>
<td>0.1390</td>
</tr>
<tr>
<td>0, 8</td>
<td>0.077 ± 0.026</td>
<td>0.1090</td>
</tr>
<tr>
<td>0, 9</td>
<td>0.050 ± 0.017</td>
<td>0.0664</td>
</tr>
<tr>
<td>0, 10</td>
<td>0.0374</td>
<td>0.0374</td>
</tr>
<tr>
<td>0, 11</td>
<td>0.0109</td>
<td>0.0109</td>
</tr>
<tr>
<td>0, 12</td>
<td>0.0023</td>
<td>0.0023</td>
</tr>
</tbody>
</table>

* Reference 52, linear interpolation from data for E_{tot} = 0.70 and 0.85 eV.

The discrepancy between the QCT and experimental partial cross sections for D + H₂ → HD + H at these relatively low collision energies may simply reflect the breakdown of classical mechanics at energies approaching threshold. Note that partial cross sections from QCT calculations for H + D₂ → HD + D at 0.55 eV relative energy are about 60% larger than those from accurate quantum calculations. The QCT results lend credence to our belief that a Feshbach resonance is present at ~0.65 eV. The QCT calculations, which should not show resonance effects, have f'_{vb} and σ(v' = 1) decreasing from 0.79 to 0.67 eV, the “normal” behavior. The experimental f'_{vb} and σ(v' = 1) increase from 0.79 to 0.67 eV, exactly opposite and precisely the expected resonance behavior.

D. Comparison with crossed molecular beam experiments

Buntin, Giese, and Gentry have reported a crossed molecular beam study of the D + H₂ → HD + H reaction in which they measured the product velocity distribution for directly backscattered product, and used this to deduce the rotational–vibrational population distributions of the backscattered HD product. The beam experiments have been done only at collision energies higher than our experiments, 0.85 to 1.20 eV, and the beam results are for product scattered into a narrow range of center-of-mass angles around 180°, while we measure the angle-averaged cross sections. Thus, the two experiments cannot be compared at the level of detail each provides. However, the results of the CARS and beam experiments are at least qualitatively the same. The 0.85 eV molecular beam data gives a broader rotational distribution than the 0.79 eV CARS data, but the mean j' values are similar. In v' = 0 we find ⟨j'⟩ = 4.8 ± 0.3, while the beam results give 5.7 ± 0.4. In v' = 1 we measure ⟨j'⟩ = 3.6 ± 0.6, while the beam results give 2.5 ± 1.7. Our spectroscopic measurements indicate that N(v' = 1)/
$N(\nu' = 0)$ is 0.092 + 0.012/ - 0.008m while the molecular beam data have this ratio equal to 0.083 + 0.028/ - 0.016.

V. CONCLUSION

We have measured relative population distributions and absolute partial cross sections for the reactive and inelastic products of D + H_2 collisions at relative collision energies of 0.67 and 0.79 eV. The observed energy disposal is similar to that in the analogous H + H_2 and H + D_2 reactions and energy transfer.

The observed increase in both the relative and absolute production of HD ($\nu' = 1$) from D + H_2 collisions that occurs upon a very small decrease in the relative collision energy from 0.79 to 0.67 eV is evidence of dynamical resonance behavior in the D + H_2 reaction. Also observed is a similar but smaller increase in the production of the inelastic H_2 ($\nu' = 1$) product at the lower energy. A dynamical, or Feshbach, resonance in this reaction just above the $\nu' = 1$ threshold would be expected to enhance the production of HD ($\nu' = 1$) and H_2 ($\nu' = 1$) from D + H_2 ($\nu' = 0$) collisions, consistent with our observations.

Quasiclassical trajectory calculations provide product quantum state distributions that are in reasonable agreement with those measured here. However, the QCT derived absolute partial cross sections are generally larger than those measured. Some discrepancy between the QCT calculations and the experimental measurements is evident even in the relative population distributions at 0.67 eV collision energy. If a dynamical resonance is influencing the dynamics at this energy such discrepancy is not unexpected.

ACKNOWLEDGMENT

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