<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Experimental study of the dynamics of D+H2 reactive and inelastic collisions below 1.0 eV relative energy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Phillips, DL; Levene, HB; Valentini, JJ</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td>The Journal Of Chemical Physics, 1989, v. 90 n. 3, p. 1600-1609</td>
</tr>
<tr>
<td><strong>Issued Date</strong></td>
<td>1989</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10722/167283">http://hdl.handle.net/10722/167283</a></td>
</tr>
<tr>
<td><strong>Rights</strong></td>
<td>This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License.; Copyright (1989) American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in (The Journal Of Chemical Physics, 1989, v. 90 n. 3, p. 1600-1609) and may be found at (<a href="http://jcp.aip.org/resource/1/jcpsa6/v90/i3/p1600_s1">http://jcp.aip.org/resource/1/jcpsa6/v90/i3/p1600_s1</a>).</td>
</tr>
</tbody>
</table>
Experimental study of the dynamics of D + H\textsubscript{2} reactive and inelastic collisions below 1.0 eV relative energy

David L. Phillips, Harold B. Levene, and James J. Valentini
Department of Chemistry, University of California, Irvine, California 92717

(Received 7 September 1988, accepted 20 October 1988)

We report the results of state-to-state dynamics experiments on the D + H\textsubscript{2} reaction as well as D + H\textsubscript{2}→H\textsubscript{2} + 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 H\textsubscript{2} 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 (v' = 1), and to a lesser extent H\textsubscript{2}(v' = 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 v' = 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 v' = 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,\textsuperscript{1-4} and is one of only a few systems for which exact three-dimensional quantum mechanical calculations\textsuperscript{5-9} are available 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\textsuperscript{10-31} focused on the H + D\textsubscript{2}→HD + D isotopic variant of the reaction and the associated rotationally and vibrationally inelastic collision process H + D\textsubscript{2}→D\textsubscript{2} + 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 + H\textsubscript{2}→H\textsubscript{2} + H isotopic variant at collision energies between 0.7 and 1.0 eV, where a rich spectrum of dynamical resonances is observed.\textsuperscript{32,33} This publication deals with the remaining easily accessible isotopic variant of the reaction, D + H\textsubscript{2}→HD + H, and the associated D + H\textsubscript{2}→H\textsubscript{2} + D inelastic collisions.

These D + H\textsubscript{2} collisions afford the only opportunity in our experiments to access collision energies not much greater than the reaction threshold. In our H + D\textsubscript{2} experiments collision energies below 0.76 eV are not accessible and for H + H\textsubscript{2} energies below 0.63 eV are not accessible, while for D + H\textsubscript{2} 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 + D\textsubscript{2}, 0.67 for H + H\textsubscript{2}, and 0.5 for D + H\textsubscript{2}, 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 + H\textsubscript{2} reaction at \( E_{\text{rel}} = 0.67 \) and 0.79 eV. These energies are not the lowest possible; exploration of the D + H\textsubscript{2} 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 + H\textsubscript{2} state-to-state dynamics experiments, which reveal pronounced dynamical resonances, Feshbach resonances, at several relative energies, including 0.70 eV.\textsuperscript{34,35} These resonances are often associated with energetic thresholds for particular product vibrational states. In the H + H\textsubscript{2} and D + H\textsubscript{2} reactions the v' = 1 thresholds are at collision energies of 0.66 and 0.61 eV respectively [for H\textsubscript{2} (v = 0, j = 0) reactant]. The opportunity to compare the state-to-state dynamics of D + H\textsubscript{2}→HD + H and H + H\textsubscript{2}→H\textsubscript{2} + H in the vicinity of a dynamical resonance seems particularly appealing. In fact, we do find evidence of a Feshbach resonance in D + H\textsubscript{2}→HD + H as well.

Even if resonance effects were absent, these lower collision energy D + H\textsubscript{2} experiments would be desirable as an...
extension of our previous $E_{\text{rel}} > 1.0$ eV $H + D_2$ studies.\textsuperscript{26-31} These $H + D_2$ 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 that $\Delta v = 1$ to $\Delta v = 0$, 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 reaction mixture between laser shots at the 10-pulse-per-second conditions. The $D_2$ photolysis waveform used in the present experiments is 266 and 280 nm, giving $D + H_2$ 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{27} 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, $\omega_{\text{as}} = 2\omega_p - \omega_s$, where $\omega_r = \omega_p - \omega_s$, is the Raman transition frequency. Edge filters and a double monochromator spectrally and spatially separate $\omega_{\text{as}}$ from $\omega_r$ and $\omega_p$. 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 $D + H_2$ 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 $D + H_2$. Previous work done under similar conditions for $H + D_2$ at $E_{\text{rel}} = 1.30$ 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.

II. EXPERIMENT

As in our previous $H + D_2$ and $H + H_2$ 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 $H_2$ products of $D + H_2$ 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. gas cell. An approximately equimolar mixture of DI/H$_2$ at 4–5 Torr total pressure flows through the sample cell at a rate (0.20 Torr cm$^{-1}$) 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 equimolar mixture 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 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 $H_2$ 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 $D + H_2$ 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{27} 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, $\omega_{\text{as}} = 2\omega_p - \omega_s$, where $\omega_r = \omega_p - \omega_s$, is the Raman transition frequency. Edge filters and a double monochromator spectrally and spatially separate $\omega_{\text{as}}$ from $\omega_r$ and $\omega_p$. 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 $D + H_2$ 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 $D + H_2$. Previous work done under similar conditions for $H + D_2$ at $E_{\text{rel}} = 1.30$ 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 $H_2$ product formed by inelastic $D + H_2$ collisions at $E_{\text{rel}} = 0.79$ eV. The thermally populated reactant $v = 0, j = 4$ state peak, and the product peaks for $v' = 0, j' = 4, 5, 6, 7, 8$, and $v' = 1, j' = 1$ 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'$1 and 1 for even $j'$1.

![FIG. 1. The vibrational Q-branch CARS spectrum of the $H_2$ product from $D + H_2$ collisions at $E_{\text{rel}} = 0.79$ eV.](image-url)
The vibrational \( Q \)-branch spectrum of HD product formed by reactive \( D + H_2 \) 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

\[
S(\omega_m) = \left( \frac{c^4}{\hbar \omega_m^2} \right)^2 (\Delta N)^2 (d\sigma/d\Omega)^2 \times \int g(\omega;\omega_m) F_2 [(f')^2 + (f''^*)^2] d\omega
+ 2 \left( \frac{c^4}{\hbar \omega_m^2} \right) (\Delta N) (d\sigma/d\Omega) \chi^{\sigma*} \int g(\omega;\omega_m) F_2 f' d\omega
\]

(2)

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 HD and HD products of \( D + H_2 \) 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 HD 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 population of the HD 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 HD \( v' = 1, j = 0 \) 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 \( H_2 (v' = 1) \) 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 \( H_2 \) 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 \( H_2 \). At the higher collision energy \( H_2 \) states up to \( v' = 0, j' = 10 \) and \( v' = 1, j' = 6 \) 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 \( v' = 0, j' = 11 \) 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 \( \pm \) 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

\[
\sigma(v',j') = \frac{\left[ H_2 (v',j') \right] / \sigma(E)}{[D] [H_2] \Delta v_{rel}}
\]

(3)

FIG. 3. Quantum state population distribution for HD formed in the D + H₂ → HD(v', j') + H reaction at a relative energy of 0.79 eV. The symbols are the experimental measurements, while the solid lines give the linear surprisal function with $\Delta_0 = 2.2$ and $\theta = 2.5$ for $v' = 0$ and 2.0 for $v' = 1$. Error bars are equivalent to $\pm$ one standard deviation.

FIG. 5. Quantum state population distribution for HD formed in the D + H₂ → HD(v', j') + H reaction at a relative energy of 0.67 eV. The symbols are the experimental measurements and the solid lines give the linear surprisal function with $\Delta_0 = 0.6$ and $\theta = 3.8$ for $v' = 0$ and 2.0 for $v' = 1$. Error bars are equivalent to $\pm$ one standard deviation.

and

\[
\sigma(v', j') = \frac{[\text{HD}(v', j')]}{([D][H_2] \Delta \nu_{\text{rel}})}, \tag{4}
\]

where [X] indicates a particle number density, $\Delta t$ is the time between the UV photolysis pulse and the CARS probe pulses, and $\nu_{\text{rel}}$ is the D + H₂ relative velocity. The collision velocity $\nu_{\text{rel}}$ is given by

\[
\nu_{\text{rel}} = \sqrt{2E_{\text{rel}}/\mu}, \tag{5}
\]

where $E_{\text{rel}}$ is the collision energy and $\mu$ is the reduced mass of D + H₂. The relative velocities are $1.25 \times 10^6 \text{ cm s}^{-1}$ for $E_{\text{rel}} = 0.79 \text{ eV}$ and $1.14 \times 10^6 \text{ cm s}^{-1}$ for $E_{\text{rel}} = 0.67 \text{ eV}$. The time delay $\Delta t$ is 5 ns. The number density of the H₂ reactant is known from a simple pressure measurement. Measurement of the CARS signals from the H₂ reactant calibrates the CARS spectral intensities and permits absolute measurement of the H₂ and HD product number densities.

The number density of deuterium atoms, [D], is given by

\[
[D] = [DI] f_{\text{photo}} f_{\text{lelec}}, \tag{6}
\]

where [DI] is the DI number density, $f_{\text{photo}}$ 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 $f_{\text{lelec}}$ is the quantum yield for the production of D + I($^2P_{1/2}$). The quantity $f_{\text{lelec}}$ is less than unity because dissociation of DI can lead to D + I($^2P_{3/2}$) or D + I($^2P_{1/2}$). For dissociation at 266 nm these two dissociation channels produce D atoms that give $E_{\text{rel}}$ of 0.79 and 0.32 eV, respectively, while dissociation at 280 nm gives $E_{\text{rel}}$ of

FIG. 4. Quantum state population distribution for H₂ product formed in inelastic D + H₂ collisions at a relative energy of 0.79 eV. The symbols are the experimental measurements and the solid line gives the linear surprisal function with $\theta = 4.4$. Error bars are equivalent to $\pm$ one standard deviation.

FIG. 6. Quantum state population distribution for H₂ product formed in inelastic D + H₂ collisions at a relative energy of 0.67 eV. The symbols are the experimental measurements, and the solid line gives the best fit linear surprisal with $\theta = 5.2$. Error bars are equivalent to $\pm$ one standard deviation.
0.67 and 0.20 eV, respectively. For 266 nm photolysis of DI, the quantum yield is 0.74 for D + I(2P\textsubscript{3/2}) and 0.26 for D + I(2P\textsubscript{1/2}).\textsuperscript{28} Photolysis of DI at 280 nm leads to greater than 95% production of the D + I(2P\textsubscript{3/2}) channel.\textsuperscript{28,29} The collision energies of the slower D atoms from the D + I(2P\textsubscript{3/2}) channel, 0.32 and 0.20 eV, are below the reaction threshold,\textsuperscript{7,12} 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\textsubscript{2} product population distributions must contain some contribution from them. However, even if the excitation cross section in D + H\textsubscript{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\textsubscript{2} product. For 0.32 eV collision energy H\textsubscript{2} states only up to \(v' = 0, j' = 6\) are accessible.

The absolute partial cross sections we derive are listed in Tables II and III. The additional cross sections needed to calculate the absolute partial cross sections lead to larger uncertainty in these distributions. 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 III: Absolute partial cross sections for D + H\textsubscript{2} → HD(\(v', j'\)) + H at 0.67 and 0.79 eV collision energy.

<table>
<thead>
<tr>
<th>(v', 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 ± 0.13</td>
<td>0.37 ± 0.12</td>
</tr>
<tr>
<td>0, 5</td>
<td>0.21 ± 0.07</td>
<td>0.20 ± 0.06</td>
</tr>
<tr>
<td>0, 6</td>
<td>0.14 ± 0.05</td>
<td>0.11 ± 0.04</td>
</tr>
<tr>
<td>0, 7</td>
<td>0.16 ± 0.06</td>
<td>0.10 ± 0.03</td>
</tr>
<tr>
<td>0, 8</td>
<td>...</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>1, 1</td>
<td>0.06 ± 0.02</td>
<td>0.04 ± 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\textsubscript{2}, \(v' = 1\) product cross sections are larger at the lower of the two collision energies. For the inelastic product the difference between the \(\sigma(v' = 1)\) at the 0.67 and 0.79 eV collision energies is within experimental uncertainty, but the \(\sigma(v' = 1)\) difference is quite large and definitely significant for the reactive product. The enhancement of \(v' = 1\) HD production relative to \(v' = 0\) 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\textsubscript{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\textsubscript{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\textsubscript{2} → 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\textsubscript{2} at 0.70 and 1.00 eV collision energy also are accompanied by an increase in \(f'_{\text{rot}}\) 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\textsuperscript{30-42} 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\textsubscript{2} reaction dynamics at different energies and for different isotopic variants of the reaction, helping to identify...
how isotopic and energetic variations alter the dynamical bias of the reaction. This is the principal advantage of the surprisal analysis, and the primary reason for our use of it. The utility of this information theory approach has been demonstrated in the analysis of our previous results for the $H + D_2$ and $H + H_2$ variants of the hydrogen exchange reaction.

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

$$P^0(v', j') = \frac{(2j' + 1)(E - E_v - E_j)^{1/2}}{\sum_j (2j + 1)(E - E_v - E_j)^{1/2}} ,$$  

(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, $\lambda_v$ and $\theta_v$, for the vibration and rotation, respectively, of the product diatom,

$$P(v', j') = P^0(v', j')\exp(-\lambda_0 - \lambda_v f_v - \theta_v g_v) .$$  

(8)

The parameters $f_v$ and $g_v$ are the fractions of the energy in vibration and rotation, $f_v = E_v/E$ and $g_v = E_j/(E - E_v)$, and $\lambda_0$ 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 $\theta_v$ may reflect the angular momentum conservation constraint that is lacking in the statistical (reference) distribution. For our purposes any such influence on $\theta_v$ 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 $E_{\text{rel}} = 0.67$ and 0.79 eV we find $\theta_v = 5.2 \pm 1.10$ 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 $\theta_v$ that we can be confident enough of to allow such extrapolation. For $D + H_2$ reactive collisions at $E_{\text{rel}} = 0.79$ eV we find linear rotational surprisal parameters $\theta_v = 2.5 \pm 0.1$ for $v' = 0$ and $\theta_v = 2.0 \pm 0.3$ for $v' = 1$. At $E_{\text{rel}} = 0.67$ eV we find $\theta_v = 3.8 \pm 0.50$ 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.

While in principle this is a serious deficiency, in practice it does nothing to diminish its usefulness, since we invoke it simply as a convenient parametrization of the product rotational state distribution. For our purposes any such influence on $\lambda_v$ does nothing to diminish its usefulness 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\cite{webster1989} indicate that the threshold for the
D + H₂ (v = 0) → HD (v' = 1) + H reaction is at 0.61 eV relative energy. These calculations also show a peak in the v' = 1 cross section and a dip in the v' = 0 cross section at ≃ 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 for DH₂ shows a well that could support the quasibound state necessary to produce the Feshbach resonance internal excitation state. In our previous experiments on H + H₂, we found a strong Feshbach resonance at 0.70 eV collision energy, about 0.04 eV above the v' = 1 product threshold, almost exactly where it was predicted theoretically. 8-11,13,48-51 The behavior expected for a Feshbach resonance just above the v' = 1 product threshold— an enhancement in the v' = 1 cross section—is precisely what we observe for both D + H₂ and H + H₂. Of course, quantum coupled channel calculations also predict a decrease in the v' = 0 product cross section at the resonance, and this we do not observe, either for D + H₂ or H + H₂. However, these calculations have been carried out only for J = 0 total angular momentum, 7-11 and, for H + H₂, for selected J < 2. 13,48-51

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 effects. Some evidence to support this view comes from an examination of the rotational distributions of the HD (v' = 1) product of the D + H₂ (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' = 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 + H₂, v' = 1 reactive cross section between 0.79 and 0.67 eV is accompanied by a similar, but smaller increase in the v' = 1 inelastic cross section. As the data in Tables I and II show, the 33% increase in the relative cross section for H₂ (v' = 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.

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

<table>
<thead>
<tr>
<th>Collision type</th>
<th>Eₜ₀</th>
<th>Reactive</th>
<th>Inelastic</th>
</tr>
</thead>
<tbody>
<tr>
<td>D + H₂</td>
<td>0.67 eV</td>
<td>v' = 0</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>v' = 1</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>0.79 eV</td>
<td>v' = 0</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>v' = 1</td>
<td>2.0</td>
</tr>
<tr>
<td>H + D₂</td>
<td>0.98 eV</td>
<td>v' = 0</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>v' = 1</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>1.10 eV</td>
<td>v' = 0</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>v' = 1</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>1.30 eV</td>
<td>v' = 0</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>v' = 1</td>
<td>2.0</td>
</tr>
<tr>
<td>H + H₂</td>
<td>0.70 eV</td>
<td>v' = 0</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>0.79 eV</td>
<td>v' = 0</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>1.00 eV</td>
<td>v' = 0</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>1.10 eV</td>
<td>v' = 0</td>
<td>5.5</td>
</tr>
</tbody>
</table>

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-H₂, H + D₂, and D + H₂, 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

Page 1606


Downloaded 04 Sep 2013 to 147.8.230.100. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://jcp.aip.org/about/rights_and_permissions
bias against rotational excitation follows the order $H + p$-$H_2 > H + D_2 > D + H_2$. 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 $H + D_2 \rightarrow HD + D$ at relative energies between 0.98 and 1.30 eV, the rotational surprisal parameters are in the range of 3.0–3.5. For $H + p$-$H_2 \rightarrow o$-$H_2 + H$ 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 $D + H_2$ system shows less bias against rotational excitation than the other two isotopic combinations. $D + H_2 \rightarrow HD + H$ 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 $\theta$, values for the $H + p$-$H_2$, $H + D_2$, and $D + H_2$ 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 $\theta$, 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 $H_2$ and $D_2$ 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 $I$, i.e., $J \approx I$. The orbital angular momentum can be related to the total cross section by the classical relation $I = \mu_{rel} b$ and $\sigma = \pi b^2$, giving

$$J \approx I = (2E_{rel}/\mu)^{1/2}(\sigma/\pi)^{1/2} = (2/\pi)^{1/2}(\mu_{rel}\sigma)^{1/2}.$$  

At a given energy the reaction cross sections are in the order $\sigma (D + H_2) > \sigma (H + H_2) > \sigma (H + D_2)$ as a consequence of zero-point energy differences, while $\mu (D + H_2) > \mu (H + D_2) > \mu (H + H_2)$. Thus, the total angular momentum available in the $D + H_2$ 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 $(\mu_{rel}\sigma)^{1/2}$, 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 $\theta$, for the inelastic collisions of the different isotopic variants we find again $H + p$-$H_2 > H + D_2 > D + H_2$.

C. Comparison with classical trajectory calculations

In Figs. 7 and 8 we compare the product quantum state distributions for $D + H_2 \rightarrow HD + H$ that we have measured with state distributions from the QCT calculations of Blais and Truhlar.\textsuperscript{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 $\Sigma_{v'} \Sigma_{j'} N(v',j')$ 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 $D + H_2 \rightarrow HD + H$ at these relatively low collision energies as they are\textsuperscript{26–33} for $H + D_2 \rightarrow HD + D$ at higher collision energies. Note that at 0.79 eV the calculations give $f_{\text{vib}}$
at 0.67 eV relative energy there are noticeable differences between the QCT results and the measurements. The calculations give a $v' = 0$ rotational distribution that seems peaked at about 1% higher than the experimental one. More importantly, the calculations give too little $v' = 1$ relative to $v' = 0$. This shows up in the average energy disposal, the trajectories giving $f'_{\text{vb}} = 0.048$, $f'_{\text{rot}} = 0.211$, and $f'_{\text{trans}} = 0.741$. This $f'_{\text{vb}}$ is only half the measured value, given in Table IV.

Comparing absolute partial cross sections (Tables VI and VII) we find that the agreement between the QCT results and the measurements is not as good. Even though the uncertainty in the absolute cross section measurements is considerable, typically $\pm 33\%$ for one standard deviation, the QCT cross sections are systematically larger than the measured values by an amount exceeding the experimental uncertainty. The only exception occurs for $v' = 1$ at 0.67 eV, for which the QCT and experimental cross sections are very close. This discrepancy is of course also reflected in the total cross sections. For the QCT data the total sections are $0.99$ and $1.23\,\text{Å}^2$ at 0.67 and 0.79 eV, while the measured values are both $0.81 \pm 0.35\,\text{Å}^2$.

Previously we found\textsuperscript{31} good agreement between QCT calculated and experimental partial cross sections for $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ at relative energies between 0.98 and 1.30 eV. Even the more accurate ($\pm 10\%$) total cross section measurements of Johnston et al.\textsuperscript{53} for $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ between 0.9 and 2.5 eV were in good agreement with the QCT total cross sections.\textsuperscript{32,33,34,35} The discrepancy between the QCT and experimental partial cross sections for $\text{D} + \text{H}_2 \rightarrow \text{D} + \text{H}$ 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\textsuperscript{32} for $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ at 0.55 eV relative energy are about 60% larger than those from accurate quantum calculations.\textsuperscript{57}

The QCT results lend credence to our belief that a Feshbach resonance is present at $\approx 0.65$ eV. The QCT calculations, which should not show resonance effects, have $f'_{\text{vb}}$ and $\sigma(v' = 1)$ decreasing from 0.79 to 0.67 eV, the “normal” behavior. The experimental $f'_{\text{vb}}$ and $\sigma(v' = 1)$ 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\textsuperscript{34,35} have reported a crossed molecular beam study of the $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ 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 $\langle j' \rangle = 4.8 \pm 0.3$, while the beam results give $5.7 \pm 0.4$. In $v' = 1$ we measure $\langle j' \rangle = 3.6 \pm 0.6$, while the beam results give $2.5 \pm 1.7$. Our spectroscopic measurements indicate that $N(v' = 1)/$

<table>
<thead>
<tr>
<th>$v'$, $j'$</th>
<th>Experiment</th>
<th>QCT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 0</td>
<td></td>
<td>0.0178</td>
</tr>
<tr>
<td>0, 1</td>
<td>0.064 $\pm$ 0.022</td>
<td>0.0523</td>
</tr>
<tr>
<td>0, 2</td>
<td>0.084 $\pm$ 0.028</td>
<td>0.0869</td>
</tr>
<tr>
<td>0, 3</td>
<td>0.089 $\pm$ 0.030</td>
<td>0.1160</td>
</tr>
<tr>
<td>0, 4</td>
<td>0.097 $\pm$ 0.033</td>
<td>0.1390</td>
</tr>
<tr>
<td>0, 5</td>
<td>0.090 $\pm$ 0.030</td>
<td>0.1570</td>
</tr>
<tr>
<td>0, 6</td>
<td>0.097 $\pm$ 0.033</td>
<td>0.1660</td>
</tr>
<tr>
<td>0, 7</td>
<td>0.074 $\pm$ 0.025</td>
<td>0.1390</td>
</tr>
<tr>
<td>0, 8</td>
<td>0.077 $\pm$ 0.026</td>
<td>0.1090</td>
</tr>
<tr>
<td>0, 9</td>
<td>0.050 $\pm$ 0.017</td>
<td>0.0664</td>
</tr>
<tr>
<td>0, 10</td>
<td></td>
<td>0.0374</td>
</tr>
<tr>
<td>0, 11</td>
<td></td>
<td>0.0109</td>
</tr>
<tr>
<td>0, 12</td>
<td></td>
<td>0.0023</td>
</tr>
<tr>
<td>1, 0</td>
<td></td>
<td>0.0053</td>
</tr>
<tr>
<td>1, 1</td>
<td>0.009 $\pm$ 0.003</td>
<td>0.0199</td>
</tr>
<tr>
<td>1, 2</td>
<td>0.009 $\pm$ 0.003</td>
<td>0.0261</td>
</tr>
<tr>
<td>1, 3</td>
<td>0.012 $\pm$ 0.004</td>
<td>0.0306</td>
</tr>
<tr>
<td>1, 4</td>
<td>0.016 $\pm$ 0.005</td>
<td>0.0224</td>
</tr>
<tr>
<td>1, 5</td>
<td>0.008 $\pm$ 0.003</td>
<td>0.0116</td>
</tr>
<tr>
<td>1, 6</td>
<td>0.007 $\pm$ 0.002</td>
<td>0.0063</td>
</tr>
<tr>
<td>1, 7</td>
<td></td>
<td>0.0024</td>
</tr>
<tr>
<td>1, 8</td>
<td></td>
<td>0.0013</td>
</tr>
</tbody>
</table>

*Reference 52, linear interpolation from data for $E_{\text{rel}} = 0.70$ and 0.85 eV.

<table>
<thead>
<tr>
<th>$v'$, $j'$</th>
<th>Experiment</th>
<th>QCT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 0</td>
<td></td>
<td>0.0229</td>
</tr>
<tr>
<td>0, 1</td>
<td>0.097 $\pm$ 0.033</td>
<td>0.0607</td>
</tr>
<tr>
<td>0, 2</td>
<td>0.100 $\pm$ 0.034</td>
<td>0.0964</td>
</tr>
<tr>
<td>0, 3</td>
<td>0.102 $\pm$ 0.035</td>
<td>0.1280</td>
</tr>
<tr>
<td>0, 4</td>
<td>0.112 $\pm$ 0.038</td>
<td>0.1400</td>
</tr>
<tr>
<td>0, 5</td>
<td>0.087 $\pm$ 0.029</td>
<td>0.1530</td>
</tr>
<tr>
<td>0, 6</td>
<td>0.078 $\pm$ 0.027</td>
<td>0.1440</td>
</tr>
<tr>
<td>0, 7</td>
<td>0.051 $\pm$ 0.021</td>
<td>0.0984</td>
</tr>
<tr>
<td>0, 8</td>
<td></td>
<td>0.0576</td>
</tr>
<tr>
<td>0, 9</td>
<td></td>
<td>0.0146</td>
</tr>
</tbody>
</table>

*Reference 52, linear extrapolation from data for $E_{\text{rel}} = 0.70$ and 0.85 eV.

$N(\nu' = 0)$ 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 + H₂ collisions at relative collision energies of 0.67 and 0.79 eV. The observed energy disposal is similar to that in the analogous H + H₂ and H + D₂ reactions and energy transfer.

The observed increase in both the relative and absolute production of HD (ν' = 1) from D + H₂ 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 + H₂ reaction. Also observed is a similar but smaller increase in the production of the inelastic H₂ (ν' = 1) product at the lower energy. A dynamical, or Feshbach, resonance in this reaction just above the ν' = 1 threshold would be expected to enhance the production of HD (ν' = 1) and H₂ (ν' = 1) from D + H₂ (ν' = 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

This work is supported by Grant Nos. CHE-8506010 and CHE-8810557 from the National Science Foundation.